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ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

II.—ON THE CONDUCT OF THE SALTS OF DIAZO-BENZENE AND OF THE THREE DIAZO-TOLUENES TOWARD ALCOHOL.

BY IRA REMSEN AND W. R. ORNDORFF.

The fact that under some circumstances diazo compounds when boiled with alcohol do not decompose in such a way as to form compounds in which hydrogen takes the place of the diazo group, has of late been frequently commented upon, but no generalisation has been reached touching the conditions which give rise to the abnormal reaction. We accordingly decided to begin a thorough investigation of the subject, with the object more particularly of discovering, if possible, the conditions which are favorable to the two kinds of decomposition of diazo compounds with alcohol. The plan which we have thus far followed, and which it is proposed to follow further, is to study with care the decomposition of a number of the simplest diazo compounds of the aromatic group. We naturally began with diazo-benzene, using both the nitrate and sulphate. We then studied the diazo compounds formed from the three isomeric toluidines. The three isomeric aniline-sulphonic acids, the nitranilines, the amido-benzoic acids, chlor-anilines, etc., will also be studied in due time, and thus, it is hoped, the material will be furnished for generalisations. In this paper the decomposition of diazo-benzene nitrate and sulphate, and of the sulphates of ortho, meta, and para-diazo-toluene is the subject treated.

Decomposition of diazo-benzene nitrate by alcohol.—Diazobenzene nitrate was made without difficulty by the method described by Griess. The crystallised compound was quickly filtered off with the aid of the pump, washed with absolute alcohol until this ran through perfectly colorless, and then with anhydrous ether. When all the wash liquid had drained off, the salt was placed on drying paper and the ether allowed to evaporate at the temperature of the room. When the odor of the ether was no longer perceptible, the salt was placed in a vacuum desiccator over sulphuric acid. Thus prepared, it is a beautiful white salt, crystallised in long needles. In dry condition it can be kept for five to six hours without undergoing change, but if kept longer it rapidly turns brown and acquires an odor resembling that of ortho-nitro-phenol.

For the decomposition with alcohol, 20 grams of pure dry diazobenzene nitrate were taken at a time. It was placed in a dry balloon flask of one litre capacity, and 200 cc. of absolute alcohol added, the flask connected with an inverted condenser, and gently heated on a water-bath. Decomposition began at a comparatively low temperature, from 50° to 60°, and was allowed to proceed without further application of heat. Nitrogen was given off freely, but no odor of aldehyde could be detected during the entire experiment. The water in the bath was finally heated to boiling, to ensure complete decomposition. 265 grams of the dry nitrate were decomposed in this way. The different portions of liquid left in the flask were united and the alcohol distilled off from a water-bath. This alcoholic distillate did not have the odor of aldehyde such as is frequently noticed in the alcoholic distillate in the case of the decomposition of a diazo compound by alcohol. It was colored slightly yellow and had a pleasant aromatic odor. On diluting it with about six times its volume of a saturated solution of sodium chloride, a light yellow oil rose to the top. This was separated, washed with caustic soda solution, then with water, dried over calcium chloride, and subjected to fractional distillation. Two colorless oils were obtained, one boiling at 80°–81°, the other at 168°–170°. The former was shown to be benzene; the latter was phenetol.

The tarry mass left in the flask after distilling off the alcohol was treated with an excess of caustic soda solution and distilled in a current of steam. A yellow oil, lighter than water and with a pleasant aromatic odor, passed over. This boiled constantly at 170° and had the other properties of phenetol.

The contents of the flask, through which steam had been passed, were then acidified with sulphuric acid and again subjected to distillation in steam. A yellow crystalline solid passed over with the steam. On purification this was found to have the melting point 45° and the other properties of ortho-nitro-phenol. The solution remaining in the flask was then filtered, boiled with bone black, evaporated to half its volume, and allowed to crystallise. The crystals after purification melted at 114° and had the general properties of dinitro-phenol.

Besides the products mentioned, a considerable quantity of tarry matter was obtained, and from this nothing with definite properties could be isolated.

As regards the quantities of the products formed in the decomposition, the result was unexpected. From the 265 grams of nitrate decomposed there were obtained 42 grams of phenetol, 5 grams of benzene, 20 grams of ortho-nitro-phenol, and 10 grams of dinitro-phenol. It will be seen that the principal reaction which takes place when diazo-benzene nitrate is decomposed with alcohol is that which gives phenetol, while that which gives benzene takes place to a very much smaller extent. In other words, in the case of the simplest aromatic diazo compound the decomposition with alcohol is for the most part strictly analogous to the decomposition with water, the two reactions being represented by the equations,

$$\frac{C_6H_5.N_2.NO_3}{OH \qquad H} = C_6H_5.OH + N_2 + HNO_3,$$

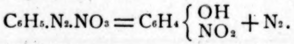
and

$$\frac{C_6H_5.N_2.NO_3}{OC_2H_5 \quad H} = C_6H_5.OC_2H_5 + N_2 + HNO_3.$$

It is evidently necessary that some of the five hydrogen atoms of the benzene should be replaced in order that the reaction shall take place in the other way.

The formation of ortho-nitro-phenol and dinitro-phenol was noticed by Griess, and he attributed their presence to the action of water, as he used ordinary alcohol. But in our experiments special care was taken to avoid the presence of water, and it is difficult to see, therefore, how phenol could first have been formed, and then converted into nitro derivatives by the action of the nitric acid liberated in the reaction.

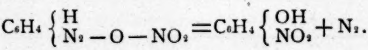
It seemed possible that the ortho-nitro-phenol might be formed by elimination of the nitrogen and a rearrangement of the constituents of the molecule without the intervention of water, as indicated in this equation,



$$C_6H_5.N_2.NO_3 = C_6H_4\left\{\begin{matrix}OH\\NO_2\end{matrix}\right. + N_2.$$

To test this hypothesis, a quantity of pure, dry diazo-benzene nitrate was decomposed by gently heating it in pure, dry toluene.

Decomposition of diazo-benzene nitrate by heating in toluene.— 15 grams of dry diazo-benzene nitrate were placed in a flask, and 250 cc. of anhydrous toluene which had been dried over sodium were added. The flask was then placed in a water-bath and the bath gradually heated. The flask must be constantly shaken and the temperature of the bath kept as low as possible. The nitrate soon began to give up nitrogen, became amorphous in form, and stuck to the sides of the flask, the toluene acquiring a deep red color. An excess of solution of sodium carbonate was then added, the toluene separated, and the sodium carbonate solution boiled for some time to get rid of toluene. The solution was placed in a large balloon flask, neutralised with sulphuric acid, and distilled with steam. A yellow crystalline solid came over. This was crystallised from alcohol and found to melt at 45°, and had the other properties of ortho-nitro-phenol. From the 15 grams of the nitrate 3 grams of ortho-nitro-phenol were obtained, and in another experiment in which 16½ grams of the nitrate were used, 4 grams of ortho-nitro-phenol were obtained. As, when the decomposition was effected in alcohol only 30 grams of ortho-nitro-phenol and dinitro-phenol together were obtained from 265 grams of the nitrate, it will be seen that a larger proportion of the nitrate undergoes this peculiar decomposition when toluene is used as the medium. These experiments make it highly probable that the formation of the substituted phenols in the decomposition of diazo-benzene nitrate with absolute alcohol is due not to the formation of phenol and the action of nitric acid upon this, but to the elimination of the nitrogen and the rearrangement of the constituents of the molecule in such a way that the linking oxygen enters the benzene molecule as hydroxyl and the nitro group takes the ortho position with reference to it:



$$C_6H_4\left\{\begin{matrix}H\\N_2-O-NO_2\end{matrix}\right. = C_6H_4\left\{\begin{matrix}OH\\NO_2\end{matrix}\right. + N_2.$$

The toluene used in the experiment was carefully examined for the presence of para-nitro-phenol, but not a trace of this was found, nor was any dinitro-phenol found.

The action of dilute (50 per cent.) alcohol on diazo-benzene nitrate was next tried, and it was found that the yield of phenetol was smaller, while that of the nitro-phenols was larger than was obtained in the experiments in which absolute alcohol had been used. The quantity of benzene formed was so small that it could not be isolated.

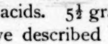
Decomposition of diazo-benzene sulphate by alcohol.—After many methods had been tried, the following was adopted for the preparation of diazo-benzene sulphate: 25 grams of the finely powdered aniline nitrate are converted into diazo-benzene nitrate, and the solution of this nitrate quickly filtered. The solution is then placed in a vessel of ice water, and an excess of concentrated sulphuric acid added, drop by drop, from a glass-stoppered burette, the flask being shaken after the addition of each drop to prevent an elevation of temperature and decomposition of the diazo compound. After adding the sulphuric acid the solution is again filtered, and then poured into twice its volume of absolute alcohol surrounded by a freezing mixture. Ether is then added until the concentrated aqueous solution of the sulphate separates in a thin layer at the bottom. The aqueous solution is then separated and again treated with alcohol and ether, and then placed in a freezing mixture. The diazo-benzene sulphate soon crystallises out, sometimes in beautiful white needles, and at others in short prisms. The crystals are filtered off and washed with absolute alcohol, and afterwards with anhydrous ether. After pressing between layers of bibulous paper, they are put in the vacuum desiccator over sulphuric acid. Thus prepared, the diazo-benzene sulphate is a beautiful white crystalline salt, very soluble in water, and almost insoluble in anhydrous ether. It is more stable than the nitrate, but like it, turns brown when kept over a day exposed to the air.

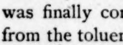
136 grams of the sulphate were decomposed in portions of about 20 grams each in the same way as the nitrate. The alcohol in which the decomposition took place did not have the odor of aldehyde. From the 136 grams of sulphate there were obtained 40 grams of phenetol and 2 grams of benzene. The yield of phenetol is therefore better with the sulphate than with the nitrate.

Phenetol.—The boiling point of phenetol is given by Boly[1] at 175°, while Cahours[2] gives it at 172°. A careful determination of the boiling point, using a carefully calibrated Zincke thermometer, gave 170°. The specific gravity, determined by means of a Mohr-Westphal balance, was found to be 0.973 at 15°. When treated with fuming nitric acid, dinitro-phenetol is very readily formed. This melts at 86°-87°, and somewhat resembles dinitrobenzene, which melts at 89.9°. As Griess obtained a compound melting at 89° on treating the oil from the alcoholic distillate with fuming nitric acid, he concluded that this was dinitro-benzene, and hence he states that benzene is the principal product of the decomposition of the salts of diazo-benzene with alcohol.

Decomposition of diazo-benzene sulphate by heating in toluene.—The formation of ortho-nitro-phenol by heating diazo-benzene nitrate in toluene suggested that a similar decomposition of the sulphate might take place, giving rise to the formation of one of the phenol-sulphonic acids. 5½ grams of the sulphate were accordingly treated as above described in the case of the nitrate, care being taken to prevent the temperature from rising above 50°. The sulphate decomposed slowly, with evolution of nitrogen, and was finally converted into a brownish heavy oil which separated from the toluene and settled at the bottom of the flask. A solution of potassium carbonate was then added and the toluene separated. The solution was then boiled to free it entirely from toluene, filtered from tarry matter, and evaporated to dryness. The residue, which consisted chiefly of potassium sulphate, was extracted several times with alcohol, and from the alcoholic solution thus obtained, short needle-shaped crystals having the general appearance of potassium para-phenol-sulphonate were deposited on evaporation. The aqueous solution of this substance gave a violet color with ferric chloride. A potassium estimation gave the following result:

0.272 gram salt gave 0.1094 gram K_2SO_4.

	Calculated for  $C_6H_4<\begin{smallmatrix}OH\\SO_3K\end{smallmatrix}$.	Found.
K	18.43	18.05

Unfortunately for our purpose, potassium toluene-sulphonate,  $C_6H_4<\begin{smallmatrix}CH_3\\SO_3K\end{smallmatrix}$, contains very nearly the same percentage of potassium as the phenol-sulphonate, and it appeared possible that the sulphuric acid set free from the sulphate might have acted upon the toluene to form the sulphonic acid. If the salt were the toluene-sulphonate, then by treating it with phosphorus pentachloride and ammonia it should easily be converted into the sulphonamide, which could be recognised by its melting point. On treating the salt in this way, however, no sulphonamide was obtained. Taking into consideration this fact, together with the color reaction with ferric chloride, the evidence that the salt is the phenol-sulphonate is fairly satisfactory.

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[1] Journal of Chemical Society **2**, 28.

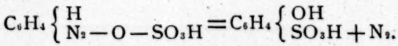
[2] Annalen der Chemie **74**, 314.

In another experiment 12 grams of the sulphate were decomposed as before in toluene. After the decomposition was complete, water and barium carbonate were added. The toluene was then poured off and the liquid boiled for some time. After filtering it was treated with bone black and again filtered. Potassium carbonate was then added until the solution had a slightly alkaline reaction; the solution filtered and evaporated to dryness. The salt thus obtained was heated for several hours to 140°–150° with an excess of benzoyl chloride. After the excess of the benzoyl chloride had been evaporated off, the dry mass was treated with ether to dissolve benzoic acid. The potassium salt was then dissolved in water and a slight excess of barium chloride solution added. A barium salt was thus obtained which was easily soluble in hot water, but almost insoluble in cold water. From the solution in hot water it was deposited in beautifully crystallised form. After recrystallisation it was found to have the properties of barium benzoyl-para-phenol-sulphonate as given by Engelhardt and Latschinoff.[1] Its analysis gave the following results:

I. 0.3272 gram salt gave 0.1097 gram $BaSO_4$.
II. 0.4092 gram salt gave 0.1377 gram $BaSO_4$.

	Calculated for $(C_{13}H_9SO_5)_2Ba$.	Found.	
		I.	II.
Ba	19.80	19.70	19.77

These results leave no doubt that when diazo-benzene sulphate is decomposed by heating in toluene it undergoes to some extent a decomposition analogous to that of the nitrate, the product being para-phenol-sulphonic acid. The change is represented in the following equation:



$$C_6H_4\begin{cases} H \\ N_2-O-SO_3H \end{cases} = C_6H_4\begin{cases} OH \\ SO_3H \end{cases} + N_2.$$

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[1] Zeitschrift für Chemie **4**, 78.

The fact that the para acid is obtained while ortho-nitro-phenol is the product of the decomposition of the nitrate is not surprising, in view of the ease with which ortho-phenol-sulphonic acid is converted into the para acid by heat.

Decomposition of ortho-diazo-toluene sulphate by alcohol.—The preparation of ortho-diazo-benzene sulphate presents no serious difficulties. The method which was found to give the most satisfactory results was the following: 25 grams pure ortho-toluidine were dissolved in 250 cc. ordinary alcohol, and an excess (25 grams) of concentrated sulphuric acid gradually added. Heat is then applied until all the ortho-toluidine sulphate has passed into solution. The flask containing the alcoholic solution is then placed in ice water and a current of nitrogen trioxide passed through it. In a short time the *o*-diazo-toluene sulphate crystallises out. It is quickly filtered off, washed with absolute alcohol until this runs through colorless, and then with anhydrous ether. When all the ether has drained off, the sulphate is placed upon bibulous paper. The salt, which when first brought on the filter is perfectly white, turns bluish green on the surface when washed with alcohol, and after the evaporation of the ether it has a tendency to turn red.

The salt was decomposed in alcohol as in the case of diazobenzene nitrate, 20 grams being used at a time. The odor of aldehyde could not be detected during the entire course of the experiment. 44 grams of the sulphate were thus decomposed. When the alcohol was distilled off on a water-bath, and diluted with about six times its volume of water, an oil rose to the top. This was separated, washed, and dried over fused calcium chloride, and found to boil at 180°. After all the alcohol was distilled off, water was added and the mixture distilled in steam. An oil which was lighter than water passed over, and this proved to be identical with that obtained from the alcohol. Its properties are those of *o*-cresol ethyl ether.[1] With nitric acid it yielded a nitro compound melting at 72°, identical with the mono-nitro derivative of the ethyl ether of ortho-cresol described by Staedel.[2] From the 44 grams of the sulphate decomposed, 13 grams of the ethyl ether were obtained, and no toluene could be detected. It is evident, therefore, that when ortho-diazo-toluene sulphate is decomposed by heating in alcohol, the principal reaction which takes place is that which yields the ethoxy derivative, and in this respect the compound acts like the salts of diazo-benzene.

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[1] Berichte der deutsch. chem. Gesell. **14**, 898.

[2] Annalen der Chemie **217**, 155.

Decomposition of para-diazo-toluene sulphate by alcohol.—Para-diazo-toluene sulphate was prepared in the same way as the ortho compound. Thus prepared it is a beautiful white salt, crystallising in thin scales or plates, having no odor and being comparatively stable. It may be kept for weeks if dry and not exposed to the light. If it is moist, or if exposed to the light, it gradually turns brown.

The decomposition in alcohol began at 75°. The odor of aldehyde was at once noticed and continued throughout the course of the experiment. 70 grams of the para-sulphate were decomposed, the residues united, and the alcohol distilled off from a water-bath. This alcoholic distillate smelled strongly of aldehyde, and an oil separated from it when about six times its volume of water was added. On purifying the oil and distilling it, it separated into two fractions, one boiling at 110°, the other at 186°–187°. By distilling in steam the residue left after the alcohol was distilled off, a further quantity of oil was obtained, which proved to be identical with the higher boiling one obtained from the alcohol. The substance boiling at 110° is toluene, the other is the ethyl ether of para-cresol,[1] as was shown by the boiling point, and by the conversion of the substance into para-ethoxy-benzoic acid,[2] melting at 195°, by oxidising with potassium permanganate.

From 70 grams of para-diazo-toluene sulphate, 13 grams of toluene and 8 grams of the ethyl ether of para-cresol were obtained. In this case, then, the presence of the methyl group in the para position to the diazo group causes the decomposition in alcohol to take place in an entirely different way from that in which it takes place when the methyl group is not present.

Decomposition of meta-diazo-toluene sulphate by alcohol.—Meta-toluidine was prepared according to the directions of Cosack,[3] by starting with para-toluidine, making the acetyl derivative, treating this with fuming nitric acid and thus making the mono-nitro derivative, eliminating the amido group, and reducing the meta-nitro-toluene by means of stannous chloride and hydrochloric acid.

The transformation of the nitro-para-toluidine into meta-nitro-toluene takes place easily and a good yield is obtained. The yield from 192 grams was 119 grams, or 68.7 per cent. This indicates that the presence of the nitro group in the meta position relatively to the methyl, and in the ortho position relatively to the diazo group, is favorable to the introduction of hydrogen in the place of the diazo group in the decomposition with alcohol.

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[1] Berichte der deutsch. chem. Gesell. **2**, 624; and Zeitschrift für Chemie, 1869, 619.

[2] Annalen der Chemie **141**, 254.

[3] Inaugural Dissertation.

The preparation of meta-diazo-toluene sulphate was carried on as follows: 18 grams of meta-toluidine were dissolved in 200 cc. of absolute alcohol, an excess (about 20 grams) of concentrated sulphuric acid added, and the flask heated until all the sulphate dissolved. The flask was then placed in ice water and a rapid current of nitrogen trioxide passed through. After some time the diazo sulphate crystallised out in small, beautiful white plates, which rapidly turned red on exposure to the air. It was filtered off, and washed first with absolute alcohol and then with anhydrous ether. On account of its instability it was decomposed at once with alcohol. This decomposition was carried on exactly as in the case of the ortho and para compounds. The odor of aldehyde was not noticed during the experiment, nor in the alcoholic distillate. From the alcoholic distillate and from the residue on heating in a current of steam, an oil was obtained which boiled at 190° and is the ethyl ether of meta-cresol.[1] This was shown to be the case by oxidising a small quantity of the oil with potassium permanganate, when it was converted into meta-ethoxy-benzoic acid[2] melting at 137°.

18 grams of meta-toluidine gave 10 grams of the ethyl ether and no toluene.

Summary.—Diazo-benzene nitrate when decomposed in alcohol yields mainly phenetol and only a very small quantity of benzene. At the same time, not inconsiderable quantities of ortho-nitro-phenol and dinitro-phenol are formed.

The substituted phenols are formed by the elimination of the nitrogen and a rearrangement of the constituents of the molecule; as was shown by the experiments on the decomposition of diazo-benzene nitrate and sulphate in toluene, para-phenol-sulphonic acid being formed in the latter case.

Diazo-benzene sulphate decomposes in essentially the same way as the nitrate, though the yield of phenetol is somewhat larger.

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[1] Berichte der deutsch. chem. Gesell. **8**, 887.

[2] Oppenheim and Pfaff, Berichte der deutsch. chem. Gesell. **8**, 888. Heintz, Annalen der Chemie **153**, 333.

When ortho-diazo-toluene sulphate is decomposed in alcohol, about 50 per cent. is converted into the ethyl ether of ortho-cresol.

When meta-diazo-toluene sulphate is decomposed, about 40 per cent. is converted into the ethyl ether of meta-cresol and no toluene is formed.

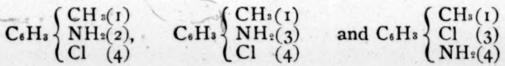
When para-diazo-toluene sulphate is decomposed, about 45 per cent. is converted into toluene and 18 per cent. into the ethyl ether of para-cresol.

The figures given are of course only approximately correct, but, as great care was taken in all the processes, they will serve to give a general idea of the course of the reactions in the cases studied.

Study of Recorded Cases.—There are on record a great many cases of the decomposition of diazo compounds by means of alcohol, and a thorough study of the literature was made in the hope of getting some clue to the law governing this kind of decomposition. Unfortunately, but few of these cases have been studied with the care which is desirable for our purpose, so that it is frequently impossible to decide whether only one product is formed or not, and in what quantity.

Our experiments appear to show that the presence of a paraffin residue in the para position relatively to the diazo group is favorable to the replacement of the diazo group by hydrogen, and that the presence of an acid group in the meta position to the paraffin residue and the ortho position to the diazo group is still more favorable to this reaction, which, for convenience, we may call the hydrogen reaction.

E. Wroblewsky[1] has called attention to the fact that, when the three isomeric chlortoluidines of the structures represented by these formulas,



$$C_6H_3\begin{cases}CH_3(1)\\NH_2(2),\\Cl\ \ (4)\end{cases}\quad C_6H_3\begin{cases}CH_3(1)\\NH_2(3)\\Cl\ \ (4)\end{cases}\quad \text{and } C_6H_3\begin{cases}CH_3(1)\\Cl\ \ (3)\\NH_2(4)\end{cases}$$

are converted into diazo compounds and these treated with alcohol, the first two yield ethoxy derivatives and the third yields meta-chlor-toluene. He concludes that "in the decomposition of the diazo compounds by alcohol, the normal reaction (i. e. the Griess or hydrogen reaction) suffers a change due to the influence of the halogen replacing the hydrogen, but only in those cases in which the halogen occupies the para position relatively to some other substituting group." In the light of our experiments on the three toluidines, it is evident that Wroblewsky's conclusion is not justified. The character of the decomposition is largely determined by the position of the diazo group relatively to the methyl group.

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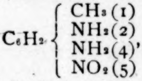
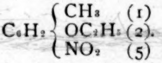
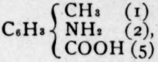
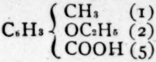
[1] Zeitschrift für Chemie **6**, 164; and Berichte der deutsch. chem. Gesell. **9**, 38, and **17**, 2703.

Ladenburg[1] obtained a compound soluble in alcohol by treating an alcoholic solution of nitro-toluylene-diamine with nitrogen trioxide. On boiling the alcoholic solution of the diazo compound thus formed, nitrogen was evolved and an ethyl ether of nitro-cresol was formed. The structure of the nitro-toluylene-diamine as shown by Staedel[2] is represented by the formula  $C_6H_2\left\{\begin{array}{l}CH_3\,(1)\\NH_2(2)\\NH_2(4)\\NO_2\,(5)\end{array}\right.$, and the ethyl ether of nitro-cresol obtained by Ladenburg has, according to Staedel, the structure  $C_6H_2\left\{\begin{array}{ll}CH_3 & (1)\\OC_2H_5 & (2)\\NO_2 & (5)\end{array}\right.$.

In this case the diazo group in the para position relatively to methyl is replaced by hydrogen, while the other, which is in the ortho position relatively to methyl, is replaced by the ethoxy group.

Schmitt[3] found that the diazo compound from para-sulphanilic acid, when boiled with alcohol under pressure, gave benzene-sulphonic acid. Ador and Meyer[4] confirm Schmitt's results and state that the yield of benzene-sulphonic acid is very satisfactory. Hybbenerth[5] has shown that the diazo compound of meta-sulphanilic acid also yields the corresponding benzene-sulphonic acid. In this case the sulpho group in the para and meta positions appear to exert the same influence whether in the para or meta position. The case of the meta acid requires further investigation.

A curious case which appears to show that the influence of methyl is stronger that that of carboxyl is that described by Remsen and Broun.[6] They showed that the diazo compound from the amido-toluic acid of the structure  $C_6H_3\left\{\begin{array}{ll}CH_3 & (1)\\NH_2 & (2)\\COOH & (5)\end{array}\right.$, is converted quantitatively into the corresponding ethoxy compound,  $C_6H_3\left\{\begin{array}{ll}CH_3 & (1)\\OC_2H_5 & (2)\\COOH & (5)\end{array}\right.$. Here, although the carboxyl is in the para position relatively to the diazo group, only the ethoxy reaction takes place, in consequence, probably, of the presence of the ortho-methyl.

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[1] Berichte der deutsch. chem. Gesell. **7**, 1212.

[2] Annalen der Chemie **217**, 155.

[3] Annalen der Chemie **120**, 153.

[4] Ibid. **159**, 9.

[5] Ibid. **221**, 205.

[6] This Journal **4**, 374.

There are on record eleven cases of amido compounds which contain besides the amido group one other substituting group, the diazo compounds of which undergo the hydrogen reaction with alcohol. Of these eleven cases, eight contain the amido group in the para position, one in the meta and two in the ortho position. The two latter are naphthalene derivatives, in which the conditions are more complicated than in the benzene derivatives.

Besides the simple cases just referred to, between eighty and ninety other cases in which two and more groups besides the amido group are present are recorded. An examination of these shows that in nearly all cases in which the hydrogen reaction takes place, the amido group is in the para position to some other group; while in most cases in which the phenetol reaction takes place, the amido group is in the ortho or meta position relatively to some other group. Many of these complex cases are, however, not well adapted to the purposes of this investigation, at least not until the simpler cases have been thoroughly investigated and the character of the influence exerted by different atoms and groups in different positions is known.

ON THE PREPARATION OF ORTHO-SULPHO-BENZOIC ACID.

By R. N. Brackett and C. W. Hayes.

For the purposes of investigations which we desired to undertake at the suggestion of Professor Remsen, a supply of ortho-sulphobenzoic acid and of benzoic sulphinide was necessary. As the methods at command for the preparation of these substances are not very satisfactory, we made a number of experiments with the object of finding, if possible, some more satisfactory method than any now known. The results obtained are described in the following paper.

Remsen and A. G. Palmer[1] endeavored to simplify the preparation of ortho-toluene-sulphonic acid by making the sulphonic acid of para-nitro-toluene, which has the constitution represented by the formula $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\ (o)\\ NO_2\ \ (p)\end{array}\right.$, and then eliminating the nitro group by means of the diazo reactions; but they found that when the diazo-sulphonic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ \left.\begin{array}{l}SO_3\\ N_2\end{array}\right>\end{array}\right.$, is boiled with alcohol, a considerable proportion of it is converted into the ethoxy compound $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\\ OC_2H_5\end{array}\right.$, and but a small quantity of the desired ortho-toluene-sulphonic acid is obtained. It was therefore determined first to try the reaction described by S. Haller, which consists in converting the diazo compound into the corresponding hydrazine compound and treating this with a dilute solution of copper sulphate.

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[1] This Journal 8, 243.

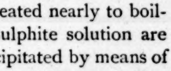
Para-nitro-toluene is easily converted into the sulphonic acid by treating it with three times its weight of fuming sulphuric acid on a water-bath. It was found convenient to make the potassium salt, as this crystallises well, and its solubility is such that it can easily be separated from its solutions.

Reduction of para-nitro-toluene-ortho-sulphonic acid.—The method of reduction first used consisted in adding ammonia to the water solution of the salt, and then saturating with sulphuretted hydrogen. On the large scale this method does not work satisfactorily, as the presence of the sulphur compounds of ammonia in the solution interfere with the complete separation of the amido acid in pure condition. It was found much better to use tin and hydrochloric acid. The reduction was conducted as follows: 5 parts by weight of the salt, 6 parts of granulated tin, and 30 parts of ordinary concentrated hydrochloric acid were placed together in a large evaporating dish. The dish was heated gently until the reaction began, then the lamp was turned out and the mixture stirred occasionally till the reaction was finished. Much heat is generated during the reduction, and the material all dissolved except some tin in excess. On cooling, a double compound of tin with the amido compound and some stannous chloride crystallised out. The crystalline mass was thrown on a filter and all the liquid drawn off as far as possible by means of a filter-pump. The double compound may be broken up and the tin removed by continued boiling with water. A better method of removing the tin consists in treating the compound with a solution of sodium carbonate. This forms a salt with the amido acid, and throws down the tin as stannous hydroxide, a white flocculent precipitate. On filtering and adding concentrated hydrochloric acid to the solution, the free amido acid is deposited in characteristic colorless rhombic crystals.

Preparation of the diazo compound.—The amido acid is easily converted into the diazo compound by suspending it in very finely powdered condition in absolute alcohol and conducting the oxides of nitrogen into the liquid, taking care to keep it cool by ice water. The success of the operation depends largely upon having the amido acid in the form of the finest powder. When the conversion is complete the granular diazo compound falls rapidly to the bottom of the liquid if the flask is shaken, whereas, as long as there is any amido acid left unchanged it remains suspended in the alcohol for a time, giving it a turbid appearance.

Preparation of the hydrazine compound.—Various methods were tried for the preparation, but that of Strecker and Römer[1] was found to give the most satisfactory results. The details of the operation are as follows:

A solution of 2.7 parts by weight of ordinary crystallised sodium carbonate in 5 parts by weight of water is saturated with sulphur dioxide, and this solution then rendered alkaline with sodium hydroxide. 100 grams of the diazo compound are gradually added to 500 cc. of the cold solution of sulphite. It turns yellow, and, after a considerable amount of the diazo compound has been added, it becomes reddish yellow. After the solution has been heated nearly to boiling for about an hour, 500 cc. more of the sulphite solution are added, and the hydrazine compound then precipitated by means of ordinary concentrated hydrochloric acid. Even while the solution is hot the hydrazine compound separates, and at the same time the solution turns yellow. On adding an excess of hydrochloric acid and allowing the mixture to cool, it solidifies to a mass of crystals. The liquid portion was drawn off by means of a filter pump, the substance washed with water and dried in the air. The substance thus obtained is the free hydrazine compound.

Hydrazine-ortho-toluene-sulphonic acid, 

$$C_6H_3\left\{\begin{array}{l} CH_3 \\ SO_3H \\ NH-NH_2 \end{array}\right.,$$

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[1] Berichte der deutsch. chem. Gesell. **4**, 784.

crystallises in lustrous scales or plates containing no water of crystallisation. It is difficultly soluble in cold water, more readily in hot water, and can be purified by crystallisation from water. It acts like an acid, dissolving in alkalies and being precipitated from the solutions by acids. It is soluble in hot concentrated sulphuric acid, but crystallises only on cooling. It has no definite melting point, but decomposes at 273°–274° (uncorr.) and then melts.

Two estimations of nitrogen and one of sulphur were made, the former by decomposing a weighed quantity of the compound with a 10 per cent. solution of copper sulphate and collecting and measuring the gas evolved, the latter by Liebig's method.

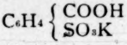
	Calculated for $C_6H_3\left\{\begin{array}{l}CH_3\\SO_3H\\NH{-}NH_2.\end{array}\right.$	Found.		
		I.	II.	III.
N	13.86	13.39	13.58	...
S	15.84	...	...	15.74.

An attempt was made to prepare the picric acid compound by treating the compound with picric acid and ether. On shaking the hydrazine compound with picric acid and ether, a solution was obtained. When the ether was allowed to evaporate, a residue was left which dissolved in hot water, and on cooling, a flocculent yellow substance separated. A crystallised compound could not be obtained.

Attempts to prepare crystallised barium and calcium salts of the hydrazine compound were unsuccessful. Both these salts are easily soluble in water and ordinary alcohol, and insoluble in absolute alcohol. Efforts to obtain ethers were equally unsatisfactory. Both when the hydrazine compound was suspended in absolute alcohol and hydrochloric acid gas passed in, and when it was boiled with concentrated sulphuric acid and absolute alcohol with a return condenser, the hydrazine compound appeared to remain unchanged.

Decomposition of the hydrazine compound with copper sulphate.—In decomposing the hydrazine compound the directions of Haller were followed. It was added to a ten per cent. solution of copper sulphate, which was then boiled. The reaction takes place without difficulty, and it can be followed by observing the evolution of nitrogen. In order to be sure that all the hydrazine compound has been transformed after all evolution of nitrogen has ceased, and no gas was evolved on adding a few drops more of copper sulphate solution, enough of the solution was added to color the liquid very slightly blue. The liquid was then filtered from the cuprous oxide, and the filtrate neutralised with chalk. After filtering off the precipitated calcium sulphate, the liquid was evaporated to a small volume, and just enough sodium carbonate added to precipitate the calcium as carbonate. The filtrate, after the removal of the calcium carbonate and calcium sulphate carried down with it, was evaporated to dryness, and the sodium ortho-toluene-sulphonate thus obtained dried on a water-bath. Although the hydrazine compound used was practically pure, the sulphonate formed from it appeared to be far from pure.

By means of the above described reactions there were obtained 655 grams of impure ortho-toluene-sulphonate from 1535 grams of pure para-nitro-toluene.

Oxidation of sodium ortho-toluene-sulphonate.—The salt is oxidised to ortho-sulpho-benzoic acid with considerable difficulty by potassium permanganate in neutral solution. Thus two experiments showed that the oxidation was not complete after twenty-four hours' boiling with an excess of permanganate. If the solution be made alkaline, however, the oxidation is completed in a few hours, yet the greatest difficulty still remains in the separation of the free acid from the products of oxidation in the solution. If hydrochloric acid be added to the solution, the acid salt  $C_6H_4\left\{\begin{matrix}COOH\\SO_3K\end{matrix}\right.$ is formed, and this has nearly the same solubility as the potassium chloride present. A better method, therefore, is to add a slight excess of sulphuric acid and evaporate nearly to dryness. In this way sulphates, and probably the free acid, are formed. The mixture is treated with 95 per cent. alcohol, which extracts the acid, leaving the greater part of the inorganic salts undissolved. This extract is evaporated and again extracted with alcohol. To this solution barium carbonate is added, the solution filtered, and just enough sulphuric acid added to precipitate the barium. The solution contained the free acid, which crystallised out on evaporation. The yield is extremely small, so that this method is not a practical one.

Formation of benzoic sulphinide from sodium ortho-toluene-sulphonate.—While pure sodium ortho-toluene-sulphonate is converted into toluene-sulphon-amide without difficulty and a good yield is obtained, the salt obtained from nitro-toluene by the reactions described above gave a very poor yield of the sulphonamide. The oxidation of the amide was conducted as recommended by Remsen and Fahlberg.[1] We obtained a rather larger yield of the sulphinide than they did, but, on the other hand, we obtained very little of the acid potassium salt, while they obtained the sulphinide and acid salt in equal quantity.

Formation of toluene-sulphon-amide by means of chlorsulphonic acid.—We next tried the method of Claesson and Wallin,[2] which has recently been successfully used by Noyes[3] for the preparation of toluene-sulphon-amide. The method works very well indeed, and is by far the most satisfactory one for the purpose. From a given weight of toluene a better yield is obtained than by any other method, and in less time than is required by other methods.

As it was found by preliminary experiment that the yield in amide by treatment of the chloride prepared by the method of Claesson and Wallin was not as was expected, attempts were made to determine the best conditions for effecting the transformation. The best results were obtained by mixing the chloride with the necessary quantity of ammonium carbonate. From five grams of the chloride three grams of amide were obtained. Besides the pure ortho-sulphon-amide and some of the para-amide, a mixture of the two, melting at 108°-120°, was obtained, and this could not be separated into its constituents. It was thought possible that the ortho-amide contained in the mixture might be obtained by treating with potassium bichromate, as Remsen has shown that the ortho-amide is oxidised with difficulty by this agent, while the para-amide is easily converted into para-sulphamine-benzoic acid. Although, after boiling for several hours with the oxidising mixture, a residue of pure ortho-amide was obtained, this was so small that it was evident that a considerable portion of the ortho as well as all of the para-amide had been destroyed. From fifteen grams of the mixture used, which, as was afterwards shown, consisted of nearly equal parts of the two amides, only three grams of the ortho-amide were recovered.

A better way to effect the separation was found to be the following: It is oxidised by means of potassium permanganate. After having evaporated the solution containing the products of oxidation, nearly neutralised with hydrochloric acid, to about one-fifth its original, it is made very slightly acid and allowed to cool. In this way nearly all the para-sulpho-benzoic acid is separated from the solution and none of the sulphinide is thrown down. After filtering, strong hydrochloric acid is added, and the sulphinide then separates in its characteristic form. This indicates that the sulphinide forms a salt with alkalies which is not decomposed by dilute hydrochloric acid, while the salt of para-sulphamine-benzoic acid is more easily decomposed. The mixture of amides melting at 105°–120° when oxidised, and the products separated in this way, gave about equal quantities of sulphinide and para-sulphamine-benzoic acid.

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[1] This Journal **1**, 426. [2] Berichte der deutsch. chem. Gesell. **12**, 1848. [3] This Journal **8**, 176.

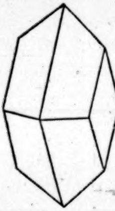
Formation of ortho-sulpho-benzoic acid from benzoic sulphinide.—Benzoic sulphinide may be converted into *o*-sulpho-benzoic acid: (1) by boiling with barium hydroxide; (2) by heating in a closed tube with concentrated hydrochloric acid; or (3) by evaporating on the water-bath with hydrochloric acid. The last method is the most convenient. The sulphinide is heated with concentrated hydrochloric acid on the water-bath for two days, the acid being from time to time renewed. Finally it is evaporated to dryness, and the residue dissolved in a small quantity of water. If the sulphinide contains any para-sulphamine-benzoic acid, as is generally the case, this is left undissolved, and most of the ammonium chloride crystallises out on standing. By slow evaporation the mother liquor deposits large colorless crystals of the free acid.

The acid is soluble in about two parts of cold water, very difficultly soluble in absolute alcohol, and almost completely insoluble in ether. It does not melt under 250°, but considerably above that it melts, at first apparently without change, and then with slight sublimation of a very deliquescent crystalline substance, possibly the anhydride.

A determination of sulphur made by Mr. A. F. Linn gave the following results:

0.1358 gram substance gave 0.1555 gram $BaSO_4 = 15.72$ per cent. S.

Calculated for the formula $C_6H_4\begin{cases} COOH \\ SO_2OH \end{cases} = 15.84$ per cent. S.



A crystallographic examination of the acid showed it to belong to the orthorhombic system.

Axial ratio, $a : b : c = 0.5507 : 1 : 0.8121$;

Planes, P and $\infty P \breve{\infty}$;

$$\text{Angles measured.}\left\{\begin{array}{l} P:P\left\{\begin{array}{lrl} \text{edge } x & = & 131^\circ\ \ 5' \\ \text{“}\ \ y & = & 82^\circ\ 18' \\ \text{“}\ \ z & = & 118^\circ\ 40' \end{array}\right. \\ P:\infty P\breve{\infty} \qquad\qquad = 114^\circ\ 38' \end{array}\right.$$

The crystals are up to 8 mm. in length. The pyramidal faces are generally etched, so that the image is poor.

INVESTIGATIONS ON THE SULPHINIDES.

VI.—ON THE ETHERS OF BENZOIC SULPHINIDE.[1]

By R. N. Brackett.

Methyl Ether of Benzoic Sulphinide.—This was prepared by treating the silver salt as well as the potassium salt of benzoic sulphinide with methyl iodide in a sealed bottle placed in a water-bath. The heating was continued for about two hours. Action takes place rapidly with the formation of silver iodide, and appears to be complete in about half an hour. After cooling, absolute alcohol is added, and the excess of methyl iodide boiled off on a water-bath. The silver iodide is then filtered off and washed with absolute alcohol. On evaporating the filtrate to a small volume and allowing to cool, crystals separate. On recrystallising these from water they melt at 131°–132°, and this does not change after repeated recrystallisations. The compound crystallises in long, flat needles. It is easily soluble in anhydrous ether, in absolute alcohol and in hot water, but difficultly soluble in cold water. It can easily be purified by crystallising from water. Three determinations of sulphur gave the following results:

I. 0.18425 gram substance gave 0.21775 gram $BaSO_4$.
II. 0.1690 gram substance gave 0.1984 gram $BaSO_4$.
III. 0.33385 gram substance gave 0.3985 gram $BaSO_4$.

	Calculated for		Found.	
	$C_6H_4\left\{\begin{array}{l}CO\\SO_2\end{array}\right\}>NCH_3$.	I.	II.	III.
S	16.24	16.23	16.13	16.39

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[1] Communicated by Ira Remsen.

Ethyl Ether of Benzoic Sulphinide.—Since the experiments described in this paper were completed, a paper by Fahlberg and List has appeared,[1] in which the ethyl ether of benzoic sulphinide, obtained by treating the sodium salt with ethyl iodide, is described. When the silver salt of the sulphinide is treated with ethyl iodide, two well crystallised products are obtained. Both crystallise in sharp, slender radiating needles. One melts at 83°–84° and the other at 96°–97°. Judging by the results obtained by Fahlberg and List, it would appear that the substance melting at the lower point is the ethyl ether of ortho-sulphamine-benzoic acid, while that melting at the higher point is the ether of the sulphinide, though Fahlberg and List give the melting point of the latter at 93°–94°, which is a little lower than I found it. The ether of ortho-sulphamine-benzoic acid could hardly have been formed in the reaction in the pressure bottle, as dry ethyl iodide and dry silver salt were used. It must have been formed in the process of purification, unless, indeed, the silver salt used was a mixture of the salts of the sulphinide and of the acid.

Propyl Ether of Benzoic Sulphinide.—This was prepared from the silver salt. The yield was not good. The product crystallised very much as the other ethers, and melted at 60°–70°.

Action of Phosphorus Pentachloride and Methyl Alcohol on Benzoic Sulphinide.—When benzoic sulphinide is mixed with an equal weight of phosphorus pentachloride and the mixture heated at 90° to 100° in a water-bath, hydrochloric acid is given off, and the mass gradually becomes semi-fluid. On cooling it does not all solidify. If the flask in which the operation is conducted be surrounded by cold water, and methyl alcohol added, hydrochloric acid is given off, much heat is generated, and a crystalline product separates. When the crystalline product is boiled with methyl alcohol it gradually dissolves. The liquid is then evaporated to a small volume, and, on cooling, crystals separate which, recrystallised from water, do not melt at 330°. From the mother liquor a small quantity of a crystalline substance melting at 123°–125° was obtained. The latter is the substance obtained by Remsen and Palmer.[2] The former is an acid, showing an acid reaction toward litmus paper in aqueous solution, and being soluble in alkalies and reprecipitated by mineral acids. The barium and calcium salts of this acid were made. They are crystallised compounds, easily soluble in water. An analysis of the calcium salt showed it to contain 7.91 per cent. water and 8.95 per cent. calcium. It was not further studied.

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[1] Berichte der deutsch. chem. Gesell. **20**, 1596.

[2] This Journal **8**, 226.

The compound melting at 123°–125° can be prepared in pure condition, and the reaction is a fairly clean one if care is taken to regulate the temperature in all the operations involved. The best result was obtained in the following way: 5 grams of benzoic sulphinide and an equal weight of phosphorus pentachloride were placed in a small Erlenmeyer flask, fitted with a cork through which passed a long glass tube. The flask was heated in a water-bath at 70°–75°. The reaction began between 65° and 70°. The heating was continued for two hours, when the mass became semi-fluid and all evolution of hydrochloric acid ceased. On cooling, all did not solidify. The flask was then surrounded with a freezing mixture of crushed ice and hydrochloric acid, and methyl alcohol gradually added from a drop-funnel. When the addition of a little methyl alcohol ceased to produce an evolution of hydrochloric acid gas, the crystalline product which had separated was boiled with methyl alcohol. The flask was then surrounded with a freezing mixture, and crystals were deposited which melted at 123°–125°. After several recrystallisations from water, the melting point rose to 125°–126° and did not change after that. If the operations are conducted as described, a good yield of this substance is obtained, and none of the substance with the high melting point.

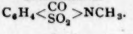
The substance melting at 125°–126° crystallises in radiating needles. It is easily soluble in alcohol, ether, and hot water. It is difficultly soluble in cold water, and can easily be purified by recrystallisation from water. Determinations of sulphur and of nitrogen gave the following results:

I. 0.2939 gram substance gave 0.2989 gram $BaSO_4$.

II. 0.1000 gram substance gave 0.1007 gram $BaSO_4$.

By Kjeldahl's method, 0.12225 gram substance gave an amount of ammonia corresponding to 5.74 per cent. N.

That the substance has not the composition of a simple ether of benzoic sulphinide is shown by a comparison of the figures:

	Calculated for	Found.	
	 $C_6H_4<\substack{CO\\SO_2}>NCH_3$.	I.	II.
S	16.24	13.87	13.83
N	7.11	5.74	...

On the other hand, a substance of the composition $C_6H_4<\substack{C(OCH_3)_2\\SO_2}>NH$ requires 13.97 per cent. sulphur and 6.11 per cent. nitrogen, figures which agree fairly well with those obtained in the analyses. From this it would appear that benzoic sulphinide has the constitution represented by the formula $C_6H_4<\substack{CO\\SO_2}>NH$, and that when phosphorus pentachloride acts upon it, the carbonyl oxygen is replaced by two chlorine atoms, forming a chloride of the formula $C_6H_4<\substack{CCl_2\\SO_2}>NH$. By the action of methyl alcohol both the chlorine atoms are replaced by methoxy groups and the compound $C_6H_4<\substack{C(OCH_3)_2\\SO_2}>NH$ formed.

A compound analogous to this was obtained by Stokes[1] by treating phthalic sulphinide successively with phosphorus pentachloride and methyl alcohol. The chloride obtained in this case had the composition represented by the formula $C_6H_3\left\{\begin{matrix}SO_2\\CCl_2\\COCl\end{matrix}\right\}N.POCl_3$, and the ether that represented by the formula $C_6H_3\left\{\begin{matrix}SO_2\\C(OCH_3)_2\\COOCH_3\end{matrix}\right\}NH$.

When the dimethyl-ether of benzoic sulphinide is boiled with water and barium carbonate, it forms a salt which proved to be the barium salt of the sulphinide. It crystallises in needles of a silky appearance, is easily soluble in water, and has the characteristic sweet taste of the salts of the sulphinide. An analysis of the air-dried salt gave 12.89 per cent. water and 23.42 per cent. barium.

	Calculated for $\left[C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right.>N\right]_2Ba+4H_2O$.	Found.
Ba	23.91	23.42
$4H_2O$	12.57	12.89

That this is really the salt of the sulphinide is shown by the fact that the sulphinide separates from it when it is treated with hydrochloric acid.

Chloride of Benzoic Sulphinide.—When the semi-fluid mass formed by the action of phosphorus pentachloride on benzoic sulphinide is cooled down with a freezing mixture, a crystalline product separates on the addition of methyl alcohol. In one experiment this crystalline product was filtered off without first boiling it with methyl alcohol. On boiling it with water to recrystallize it, the sulphinide was obtained and no methyl compound. This was probably the chloride. On preparing some of it in the way described, it was found to contain chlorine. An attempt was made to recrystallise it from petroleum ether, but it is very slightly soluble. After boiling with petroleum ether the compound was sweet, though it still contained chlorine. Fearing, however, that some decomposition had taken place, no analysis was made. In another experiment, anhydrous ether was used for the purpose of isolating the chloride. The crystalline product was carefully washed repeatedly with anhydrous ether to remove all the phosphorus oxychloride, and then placed over calcium chloride in a desiccator. Determinations of chlorine gave varying results, and none that agreed with those required by the formula $C_6H_4\left\{\begin{matrix}CCl_2\\SO_2\end{matrix}\right. > N.POCl_2$. Lack of time and material prevented a further examination of the substance.

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[1] This Journal **6**, 275.

The facts brought to light in this investigation speak in favor of the formula $C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right. > NH$ for benzoic sulphinide. Further, the evidence furnished by the work of Fahlberg and List[1] is also in favor of the same formula.

P-AMIDO-*O*-SULPHO-BENZOIC ACID.

By W. A. Hedrick.

Of the ten isomeric substances of the formula $C_6H_3\left\{\begin{matrix}NH_2\\SO_3H\\CO_2H\end{matrix}\right.$, four, or perhaps five, are known. The first one was described by Limpricht and Uslar.[2] They obtained it by treating *m*-sulphobenzoic acid with nitric acid and sulphuric acid, and reducing the nitro acid with hydrogen sulphide. By heating *m*-amido-benzoic acid with sulphuric acid, Griess[1] obtained two acids which can be separated by means of the barium salts. By reducing *m*-nitro-*p*-sulpho-benzoic acid, Hart[2] obtained the corresponding amido acid. This is probably identical with one of the acids described by Griess. Hart also made *o*-amido-*p*-sulpho-benzoic acid and *p*-amido-*o*-sulpho-benzoic acid from the corresponding nitro-compounds. In the course of some other investigations the preparation of this last acid became necessary, and I therefore undertook a study of the best conditions for its preparation, as well as of the acid itself and some of its derivatives.

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[1] Loc. cit.

[2] Annalen der Chemie **106**, 79.

Preparation.—The potassium salt of *p*-nitro-*o*-toluene-sulphonic acid was first made, and this subjected to oxidation by means of potassium permanganate. The best proportions are as follows: Ten parts potassium salt, 3 parts potassium hydroxide, 22 parts permanganate, and 500 parts water. The permanganate and hydroxide are dissolved in the requisite quantity of water and the salt added. The whole is then heated in a water-bath with occasional shaking, until the permanganate is completely reduced and the liquid has a yellow color. The precipitated oxides of manganese are filtered off, the solution nearly neutralised with hydrochloric acid, and evaporated until a portion nearly solidifies when treated with hydrochloric acid. The whole solution is then acidified and, after cooling, filtered. The precipitate thus obtained is the acid potassium salt of *p*-nitro-*o*-sulpho-benzoic acid, $C_6H_3\left\{\begin{array}{ll}COOH & (1)\\ SO_2OK & (2)\\ NO_2 & (4)\end{array}\right.$. There is some loss in this process, but the yield is fairly good.

The nitro-compound is best reduced by dissolving the acid potassium salt in dilute ammonia and, while keeping the solution gently warmed, passing in hydrogen sulphide. A little ammonia is added from time to time, but a large excess must be avoided. During the reduction the solution changes color. The solution is filtered from precipitated sulphur, evaporated to dryness, the residue dissolved in water and acidified with hydrochloric acid. The amido acid is then precipitated in semi-crystalline form. It is further purified by dissolving in a dilute solution of sodium carbonate, again filtering and precipitating. It is then recrystallised from water. As regards the yield of the pure acid, it was found to be about half the weight of the nitro-toluene used.

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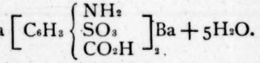
[1] Journal für prak. Chemie [2], **5**, 244.

[2] This Journal **1**, 340.

Salts of the Amido Acid.—The only salts of the acid mentioned by Hart are the ammonium and neutral barium salts. To obtain the barium salt, ten grams of the amido acid were boiled in a flask with barium carbonate. A soluble salt was first formed, but on continued boiling in the presence of barium carbonate, an insoluble compound is formed. Believing that the salt had become dehydrated by boiling, a part of the precipitate was transferred to a large flask, a large quantity of water added, and the contents boiled for an hour. The solution was then filtered, but only very little had passed into solution. To obtain the soluble salt the boiling was stopped, and the excess of barium carbonate filtered off before the insoluble salt was formed.

Acid Barium Salt.—This salt, made as indicated above, separated from the solution on cooling. The crystals were small columns; they are quite easily soluble in hot water, but much less in cold water. They are insoluble in alcohol, and blacken slightly on long exposure to light and air. No definite results could be obtained in determining the water of crystallisation, but judging by the percentage of barium found, the composition of the crystals is represented by the formula



$$\left[C_6H_3\left\{\begin{array}{l}NH_2\\SO_3\\CO_2H\end{array}\right.\right]_2Ba + 5H_2O.$$

I. 0.3170 gram salt gave 0.1130 gram $BaSO_4$.

II. 0.2537 gram salt gave 0.0909 gram $BaSO_4$.

	Calculated for $(C_6H_3.NH_2.CO_2H.SO_3)_2Ba + 5H_2O$.	Found. I.	II.
Ba	20.92	20.96	21.07

The difficulty in determining the water of crystallisation was due to the fact that the salt is comparatively easily decomposed by heat.

Lead Salt.—The lead salt was prepared, but it could not be obtained in pure condition. The analysis gave the following results:

I. 0.4349 gram salt gave 0.3199 gram $PbSO_4$.

II. 0.3542 gram salt gave 0.2603 gram $PbSO_4$.

	Calculated for $(C_6H_3.NH_2.CO_2.SO_3)Pb$.	Found. I.	II.
Pb	48.96	50.25	50.23

The neutral ammonium salt was made by dissolving the acid in a small quantity of ammonia and evaporating to dryness on a water-bath. It was hoped that from this the lead, zinc and magnesium salts might be obtained by double decomposition with lead acetate, zinc and magnesium sulphates. But nothing was precipitated, nor did the salts crystallise out on evaporating to a small volume.

Silver Salt.—By adding silver nitrate to the solution of the neutral ammonium salt a precipitate is formed. This is a white powder, practically insoluble in hot and cold water, but decomposed by nitric acid. The analyses gave the following results:

I. 0.4264 gram salt gave 0.2786 gram AgCl.

II. 0.2854 gram salt gave 0.1865 gram AgCl.

	Calculated for $C_6H_3.NH_2.CO_2Ag.SO_3Ag$.	Found.	
		I.	II.
Ag	50.11	49.19	49.24

Methyl-amido-sulpho-benzoic Acid.—The silver salt of amido-sulpho-benzoic acid was treated with methyl iodide and methyl alcohol in a closed vessel at the temperature of the water-bath. After expelling the excess of the liquid reagents, the residue was immediately boiled with water. The solution thus obtained had a dark color, which was only partially removed by boiling with animal charcoal. It was boiled with finely powdered calc spar and filtered. On standing for some time, small crystalline particles were deposited. These were separated and further purified by crystallisation. They are not easily soluble, were of a dark color, and do not appear homogeneous. The results of the analyses are as follows:

I. 0.1284 gram salt gave 0.0626 $CaSO_4$.

II. 0.1953 gram salt gave 0.0936 $CaSO_4$.

	Calculated for $C_6H_3\left\{\begin{array}{l}N(CH_3)_2\\CO_2\\SO_3\end{array}\right.>Ca$.	Found.	
		I.	II.
Ca	14.13	14.34	14.38

The reaction between the silver salt and methyl iodide may be represented thus:

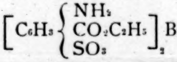
$$C_6H_3\left\{\begin{array}{l}NH_2\\SO_3Ag\\CO_2Ag\end{array}\right. + 2CH_3I = C_6H_3\left\{\begin{array}{l}N(CH_3)_2\\SO_3H\\CO_2H\end{array}\right. + 2AgI.$$

With ethyl iodide the silver salt appears to act differently. The product obtained, which consisted of a gummy mass, was boiled with water and barium carbonate. On cooling, a white crystalline substance was deposited. This could easily be recrystallised from water. The analysis gave the following results:

0.1630 gram salt gave 0.0605 gram $BaSO_4$.

	Calculated for $(C_6H_3.NHC_2H_5.CO_2H.SO_3)_2Ba$ or $(C_6H_3.NH_2.CO_2C_2H_5.SO_3)_2Ba$.	Found.
Ca	21.82	21.92

As the salt appeared to be neutral, the formula



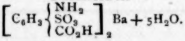
$$\left[C_6H_3\begin{cases}NH_2\\CO_2C_2H_5\\SO_3\end{cases}\right]_2Ba$$

is the more probable.

Attempts to prepare Acetyl and Benzoyl Compounds of the Amido Acid.—The amido acid was heated for about two hours with acetic anhydride in a flask connected with an inverted condenser. On getting rid of the acetic acid it was found that no action had taken place, the original acid being obtained unchanged, as was shown by its solubility and the properties of the soluble barium salt. Further, the crystallised barium salt was analysed, with the following results:

I. 0.2172 gram salt gave 0.0776 gram $BaSO_4$.

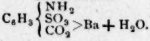
II. 0.2675 gram salt gave 0.0945 gram $BaSO_4$.

	Calculated for  $\left[C_6H_3\begin{cases}NH_2\\SO_3\\CO_2H\end{cases}\right]_2Ba + 5H_2O$.	Found.	
		I.	II.
Ba	20.92	21.01	20.80

The neutral barium salt was made also by adding barium chloride to a solution of the neutral ammonium salt. It was analysed with the following results:

I. 0.1915 gram salt lost 0.086 gram H_2O and gave 0.1205 gram $BaSO_4$.

II. 0.1062 gram salt lost 0.047 gram H_2O and gave 0.067 gram $BaSO_4$.

	Calculated for  $C_6H_3\begin{cases}NH_2\\SO_3\\CO_2\end{cases}>Ba + H_2O$.	Found.	
		I.	II.
Ba	36.98	37.00	37.09
H_2O	4.87	4.5	4.43

A portion of the acid was heated with benzoyl chloride in an oil-bath to 150° for three hours. At no time was the evolution of any considerable quantity of hydrochloric acid noticed. On getting rid of the benzoyl chloride, nothing but the unchanged amido acid was obtained.

In this case the basic properties of the ammonia residue are entirely destroyed by the presence of the sulphonic acid group in the ortho position, and the nitro group in the para position.

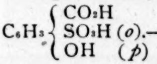
Diazo Compound.—The diazo compound corresponding to *p*-amido-*o*-sulpho-benzoic acid is mentioned by Remsen and Palmer,[1] but they give no directions for preparing it, nor do they describe it. Three methods were tried. First, the amido acid was suspended in water kept cold by surrounding it with ice, and the oxides of nitrogen conducted into the liquid. After some time the liquid was filtered off and examined, but there was practically nothing in solution. The solid portion exploded when gently heated, and decomposed with an evolution of nitrogen when boiled with water, but it did not decompose with alcohol. Second, the ammonium salt of the amido acid was made, and nitrous acid fumes conducted into the solution. It changed color, and in about half an hour a crystalline substance was deposited. This was filtered, washed and dried, and was shown to be the diazo compound. The best way to prepare the diazo compound, however, is to conduct nitrous fumes into an aqueous solution of the acid barium salt of the amido acid in which some of the salt is suspended. Generally, in the course of about twenty minutes a white crystalline homogeneous mass is deposited. This is whiter than the diazo compound prepared in the other ways. The nitrogen in the diazo compound prepared from the ammonium salt, and in that from the barium salt, was determined by boiling with water in an atmosphere of carbon dioxide and collecting the gas over caustic alkali. Determinations I and II were made with the compound from the barium salt; determination III with the compound from the ammonium salt.

I. 0.6999 gram compound gave 74.32 cc. N at 17.8° and 764.8 mm.

II. 0.5963 gram compound gave 64.58 cc. N at 20° and 758.8 mm.

III. 0.4826 gram compound gave 48.41 cc. N at 20° and 758.7 mm.

	Calculated for $C_6H_3\begin{cases}N_2 > \\ SO_3 \\ CO_2H.\end{cases}$	Found. I.	 II.	 III.
N	12.28	12.31	12.24	11.42.



Hydroxy-sulpho-benzoic Acid, $C_6H_3\begin{cases}CO_2H \\ SO_3H\ (o) \\ OH\ \ (p)\end{cases}$.—This acid was prepared by boiling the diazo compound with water. On evaporating to dryness, a red gummy mass was obtained. A concentrated solution was placed under a bell jar over sulphuric acid and allowed to evaporate spontaneously. Impure crystals were obtained. These deliquesced when exposed to the air. To the concentrated aqueous solution of the acid, alcohol and ether were added successively, but nothing was precipitated.

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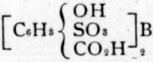
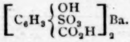
[1] This Journal 8, 251.

Barium Hydroxy-sulpho-benzoate,  $\left[C_6H_3\left\{\begin{matrix}OH\\SO_3\\CO_2H\end{matrix}\right.\right]_2Ba$. — This salt was prepared by boiling the aqueous solution of the acid with barium carbonate. A soluble salt was formed at first, but by continued boiling with barium carbonate an insoluble salt was formed. This insoluble salt is insoluble in an excess of the hydroxy acid, and in dilute acetic acid, but soluble in dilute hydrochloric acid. When the solution of the soluble salt is evaporated to a small volume it does not deposit crystals, but the salt separates in the form of a powder. The analyses gave the following results:

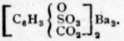
I. 0.2506 gram salt gave 0.0894 gram $BaSO_4$.
II. 0.2048 gram salt gave 0.0753 gram $BaSO_4$.



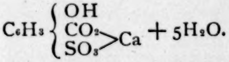
	Calculated for $\left[C_6H_3\left\{\begin{matrix}OH\\SO_3\\CO_2H\end{matrix}\right.\right]_2Ba$.	Found. I.	II.
Ba	23.97	22.02	22.76

The neutral barium salt was made by adding barium chloride to a solution of the neutral ammonium salt. The analyses gave the following results:

I. 0.6230 gram salt gave 0.5178 gram $BaSO_4$.
II. 0.4898 gram salt gave 0.4062 gram $BaSO_4$.



	Calculated for $\left[C_6H_3\left\{\begin{matrix}O\\SO_3\\CO_2\end{matrix}\right.\right]_2Ba_3$.	Found. I.	II.
Ba	48.80	48.80	48.76

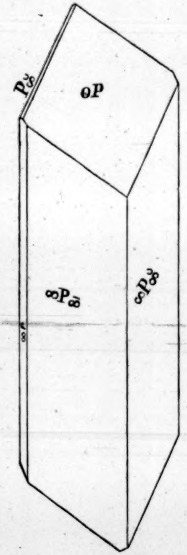
Calcium Hydroxy-sulpho-benzoate,  $C_6H_3\left\{\begin{matrix}OH\\CO_2\\SO_3\end{matrix}\right.\!\!>Ca + 5H_2O$. —The calcium salt was prepared by boiling the aqueous solution of the acid with finely powdered calcium carbonate. It is fairly easily soluble in hot water, but less in cold. It crystallises in beautiful columns, though sometimes radiating masses were obtained. The analyses gave the following results:

I. 0.3947 gram salt lost 0.1026 gram H_2O and gave 0.1548 gram $CaSO_4$.

II. 0.3187 gram salt lost 0.0799 gram H_2O and gave 0.1250 gram $CaSO_4$.

	Calculated for $C_6H_3\left\{\begin{matrix}OH\\CO_2\\SO_3\end{matrix}\right. > Ca + 5H_2O$.	Found. I.	II.
Ca	11.57	11.58	11.53
H_2O	26.01	26.00	25.75

The water is not driven off under about 185°.



Mr. A. C. Gill, a student in mineralogy in this university, has kindly furnished me with the following information regarding the crystals of the salt :

"The crystals are triclinic, elongated in the direction of the vertical axis.

"Axial ratio $\breve{a} : \bar{b} : c' = 0.9567 : 1 : 1.0121$.

"The angles obtained by taking the mean of the measurements of several crystals are as follows :

$\infty P \bar{\infty} \wedge \infty P \breve{\infty} = 129^\circ\ 11'$
$\infty P \bar{\infty} \wedge 0P = 134^\circ\ 25'$
$\infty P \breve{\infty} \wedge 0P = 140^\circ\ 52'$
$P \breve{\infty} \wedge 0P = 115^\circ\ 14'$
$\infty P \bar{\infty} \wedge \infty P = 110^\circ\ 32'$

"Though the crystals are quite brittle, no definite cleavage could be determined. The rounding of the faces on most of the crystals gave a large variation in the angles, but the more perfect faces gave agreeing results."

Hydrazine Compound.—To prepare the hydrazine compound, the diazo compound was added to a cold saturated solution of neutral sodium sulphite. At first the solution turned reddish yellow, and then became golden yellow. When the diazo compound had completely dissolved, the solution was boiled and hydrochloric acid was added. Soon a crystalline deposit was formed. The yield was fairly good. The hydrazine compound obtained in this way crystallises in small white needles which are not very soluble in cold, but more readily in hot water, from which it crystallises on cooling. It readily reduces copper and silver salt solutions.

A small quantity was boiled with a dilute solution of copper sulphate and a substance which had the general properties of ortho-sulpho-benzoic acid was obtained, though other substances were formed at the same time.

The hydrazine compound has acid properties, and when its solution is boiled with barium carbonate, a soluble barium salt is formed, which is deposited from the solution in the form of sharp pointed needles.

The work described above was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

JOHNS HOPKINS UNIVERSITY, *June*, 1887.

Communication from the Chemical Laboratory of Rutgers College.

XIV.—A CONVENIENT FORM OF GAS RECEIVER FOR USE IN GAS ANALYSIS BY THE ABSORBIOMETRIC METHOD.

BY FRANCIS A. WILBER.

In following out the method for determining dissolved gases, in the analysis of potable water, as given by Prof. J. W. Mallet in his report to the National Board of Health,[1] difficulty was experienced in handling the gases after they were collected. Prof. Mallet used for this purpose a Cooper's receiver, see Fig. 1, with a modified form of stopper. The introduction into this receiver of the absorbent solutions was attended with some trouble, and to obviate this, the receiver described below, Fig. 2, was devised.

This receiver consists of two parts, *A* and *B*, connected by the rubber tube *T*. The part *A* is divided into two parts by the large and accurately ground stop-cock *C*. The upper portion *D* is graduated from *C* upward into one-tenth cc. It is used to contain the absorbent solutions while they are being introduced into the lower portion *E*. *E* is graduated, from *C* downward, into one-tenth cc. The receiver has a capacity of 50 cc. The two

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[1] Report of National Board of Health for 1882, pp. 284–286.

Fig. 1.

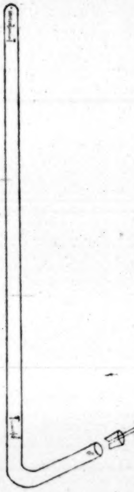
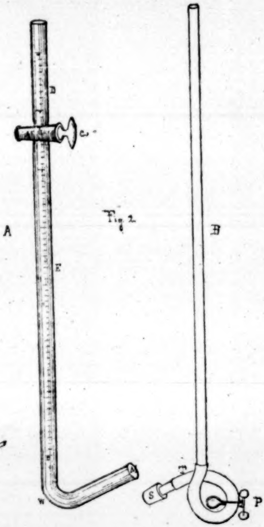


Fig. 2.



parts *A* and *B* are supported in clamps in a vertical position; *E* is completely filled with mercury before it is brought into position. A sheet-iron pan is put beneath them to catch the overflow of mercury. The mixture of gases to be analysed is then introduced into *E;* the tip of the tube, which delivers the gases, being thrust through the mouth *M* until it touches the wall of the receiver at *W*. After the gases are introduced the stopper *S* is forced tightly into *M*, and mercury is poured into *B*, the pinch-cock *P* being open until the level of mercury is the same in *E* and *B*. The volume of the enclosed gases is then read and temperature and pressure noted. The pinch-cock is now shut, the stopper *S* removed from *M*, and the first absorption made. In water analyses, where oxygen, carbonic acid and nitrogen are the gases determined, the absorbent solutions are caustic soda for carbonic acid and alkaline solution of pyrogallol for oxygen. The residual gas is taken for nitrogen. The caustic soda solution used had a specific gravity of 1.05, as recommended by Weil and Zeitler,[1] and 10 cc. were used for each absorption.

It is put in *D*, the cock *C* cautiously opened a little, and the solution allowed to run slowly down. Absorption takes place rapidly as the gases are washed by the flowing solution. With care the absorbent can be run in to the last one-tenth cc. without danger of admitting air. After admitting the caustic soda, *S* is replaced in *M*, *P* is opened, and the mercury in *B* brought to the proper level. This level is one-thirteenth of the distance occupied by the caustic soda in *E* above the mercury level of *E*. Any air under *S* is allowed to escape through *B* before the level is made, and after standing 15-20 minutes the reading is taken, and thermometer and barometer read. *P* is again closed, *S* removed from *M*, and the solution of pyrogallol is quickly introduced into the receiver. The charge used for oxygen absorption is 0.5 gram solid pyrogallol dissolved in 10 cc. of the above-mentioned caustic soda solution. It is exposed to the air as short a time as possible.

After this is introduced, *S* is replaced in *M*, *P* opened, the mercury in *B* brought to its proper level, and a third reading taken. From these three readings, when corrected for temperature and pressure, the oxygen, carbonic acid, and nitrogen are determined. Excellent results were obtained with the receiver when samples of atmospheric air were analysed.

The labor demanded in making such absorptions in gas analysis is much reduced by the use of this receiver. It will be found to be a simple and easily managed form of apparatus for rapid work.[2]

NEW BRUNSWICK, N. J., *July* 16, 1887.

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[1] Liebig's Annalen **205**, 255.

[2] The apparatus may be obtained of Emil Greiner, 79 Nassau Street, New York.

Contributions from the Chemical Laboratory of Wesleyan University.

V.—ON THE CHEMISTRY OF FISH.

PART I.—ANALYSES OF SPECIMENS OF AMERICAN FISHES.

BY W. O. ATWATER.

The Commissioner's Reports of the United States Commission of Fish and Fisheries for 1880 (Washington, 1883) and 1883 (Washington, 1885) have contained accounts of the progress of an investigation of the chemical composition and nutritive values of American food-fishes and invertebrates. A monograph including detailed results of this research up to the present date is now in preparation, and, it is expected, will be published by the Commission. Awaiting this monograph, the present article and others which may follow are intended to epitomise some of the principal results.

The investigation in its present status includes:

I. Chemical analyses of the flesh of American food-fishes and invertebrates.

II. Experiments upon the digestibility of the flesh of fish.

III. Studies of the chemical constitution of the albuminoids of the flesh of fish.

Analyses have been made of flesh of American fishes, 122 specimens belonging to 52 species; of flesh of European fishes, 3 specimens of 2 species; of flesh, etc., of American invertebrates, 64 specimens of 11 species.

Two of the European specimens were of a species included in the American fishes. The total number of specimens of fish analysed is, therefore, 125, belonging to 53 species. These, with the invertebrates, make 189 specimens belonging to 64 species. Since, in numerous cases, analyses were made of more than one part of the specimen, the actual number of analyses is larger than these figures imply.

I am informed by gentlemen connected with the United States Fish Commission that nearly one thousand different species of fish are used for food in the United States. When we consider that almost no other analyses of American food-fishes have been made (I am aware of but two); that different specimens of the same species vary considerably in composition, so that several analyses of each are necessary to show the ranges of variation and the average composition in the different circumstances of locality, season, size, age, sex, etc.; and that, from both the chemical and economical standpoints, studies of the constitution of the ingredients of the flesh and of other tissues are needed to make our information at all complete, it is evident that the work here reported can be regarded as only the beginning of a much needed research.

Along with these studies, a series of analyses of meats, dairy products, and other food materials, animal and vegetable, have been undertaken at the instance of the United States National Museum, to furnish data for illustrating and explaining its food collections. These analyses, though not specifically a part of the investigation herewith reported, form an important economical supplement to it, because of the desirability of data for comparisons of fish with other foods. The number of analyses of the latter kind already made is about ninety.

While the work has been constantly under my immediate supervision, and much of it has been done by myself, the larger part of the details have been skilfully and faithfully performed by my assistants, Messrs. G. P. Merrill, W. H. Jordan, J. H. Long, Miles Beamer, E. B. Voorhees, E. W. Rockwood, and especially C. D. Woods.

I.—Names and Synonyms of American Fishes Analysed.

Of the specimens of fishes analysed, a considerable number were found in fish markets in Middletown, Conn. These were mostly of common species whose names were well known to us. By far the larger number were supplied through the kindness of Mr. E. G. Blackford, Fish Commissioner of the State of New York, who gave with each specimen the common name and in some cases the Latin name. Specimens with which we were not familiar, or the names of which were for other reasons a matter of doubt, were referred to Prof. W. N. Rice, of this college, who was so kind as to either identify them himself or have them identified under his supervision. Prof. Rice tells me that the specific differences are sometimes difficult to distinguish, especially in specimens that are not entirely normal or have been distorted in packing and transport, so that it is not impossible that errors have been made. I cannot believe, however, that with the literature of the subject and many typical specimens in the college museum conveniently at hand and freely used, many or serious mistakes could have occurred. Some doubtful cases are indicated in the explanations and tabular statements beyond.

The selection of names and the classification of the specimens has been a perplexing matter, on account of the differences in usage of ichthyologists as to both the generic and specific names which should be applied to a given species, even the same authority insisting on different names for a given species in different writings.

In accordance with the suggestion of my colleagues, Professors Rice and Conn, the names given in Jordan and Gilbert's Synopsis of the Fishes of North America[1] have been adopted, except in a few cases in which other names, generally those employed in previous, have been used.

I am under obligations, not only to the gentlemen named, but also to Prof. D. S. Jordan for assistance in the preparation of the following list of synonyms, which is simply for the convenience of chemists and others to whom the variations in current terminology are perplexing. Where the French and German names of the species which occur in Europe were known to me, they have been inserted.

The order of arrangement here and in some of the principal tabular statements of analyses follows, in the main, that of Jordan and Gilbert.

Sundry matters regarding identification, names, etc., will be spoken of in more detail in the monograph referred to above.

LIST OF NAMES OF FISHES.

Acipenser sturio. Common sturgeon ; Fr., Esturgeon ; Ger., Stör. No. 238.

Moxostoma velatum. Small-mouthed red horse ; Buffalo fish. No. 258.

Clupea harengus. Common herring ; Whitebait (young) ; Fr., Hareng ; Ger., Häreng. Nos. 33, 47.

Clupea pilchardus (?). Sardine ; Pilchard ; Fr., Sardine ; Ger., Pilchard. No. 87.

Clupea vernalis ; Clupea mattowscea, Günther. Alewife ; Branch herring ; Gaspereau. Nos. 5, 220.

Clupea sapidissima. Common shad. Nos. 6, 10, 32, 212, 221, 245, 249.

Osmerus mordax ; O. viridescens, Günther. American smelt. Nos. 23, 207.

Coregonus clupeiformis ; C. albus, Günther. Common white fish. No. 18.

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[1] Bulletin of the U. S. National Museum, No. 16.

Coregonus sp. (*tullibee* or *artedi?*). Cisco; Lake herring. No. 111.

Oncorhyncus chouicha; O. quinnat, Günther. California salmon; King salmon; Columbia salmon; Sacramento salmon; Chinnook salmon; Tyee salmon; Saw-kwey; Chouica. Nos. 27, 29, 96, 233, 241.

Salmo salar. Common Atlantic salmon; Fr., Saumon; Ger., Lachs, Salm. Nos. 14, 77, 78, 279, 280, 35, 36.

Salmo salar subsp. sebago. Land-locked salmon. Nos. 40, 41.

Salvelinus namaycush; Salmo namaycush, Günther. Lake trout; Mackinaw trout; Great lake trout; Longe (Vermont); Togue (Maine). Nos. 17, 255.

Salvelinus fontinalis; Salmo fontinalis, Günther. Brook trout; Speckled trout. Nos. 24, 254, 256.

Esox reticulatus. Common eastern pickerel; Green pike. Nos. 100, 224.

Esox lucius. Pike, Pickerel (Vermont, New York, etc.); Fr., Brochet; Ger., Hecht. No. 98.

Esox nobilior. Mascalonge; Muskallunge; Musquallonge; Maskinonge. No. 45.

Anguilla rostrata; A. Bostoniensis, Günther. Common eel. Nos. 4, 217.

Mugil albula; M. lineatus, Günther. Striped mullet. No. 126.

Scomber scombrus; Scomber scomber, Günther. Common mackerel; Fr., Macquereau vulgaire; Ger., Makrele. Nos. 8, 13, 30, 39, 42, 94, 95, 219, 230, 261.

Cybium maculatum, Günther; *Scomberomorus maculatus*, Jor. and Gil. Spanish mackerel. No. 43.

Trachynotus carolinus; T. pampanus, Günther. Common pompano. Nos. 234, 263.

Pomatomus saltator; Temnodon saltator, Günther. Blue fish; Green fish; Skip jack. No. 12.

Stromateus triacanthus. Butter fish; Dollar fish; Harvest fish; La Fayette. No. 90.

Micropterus salmoides; Huro nigricans, Günther. Large-mouthed black bass; Black bass; Oswego bass; Green bass; Bayou bass. No. 53.

Micropterus dolmieu; Grystes fasciatus, Günther. Small-mouthed black bass. No. 91.

Perca fluviatilis; (vid. Günther, Study of the Fishes, p. 375, and Jor. and Gil. p. 524); *Perca americana*, Jor. and Gil. Yellow perch; American perch; Ringed perch; Perch. Nos. 127, 208.

Stizostedium vitreum; Lucioperca americana, Günther. Pike perch; Wall-eyed pike; Dory; Glass eye; Yellow pike; Blue pike; Jack salmon. No. 52.

Stizostedium canadense, Jor. and Gil.; *Lucioperca canadensis*, Günther. Pike perch; Gray pike; Sanger; Sand pike; Horn fish. No. 257.

Roccus lineatus; Labrax lineatus, Günther. Striped bass; Rock fish; Rock. Nos. 7, 19, 225, 237, 248, 260.

Roccus americanus; Labrax rufus, Günther. White perch. Nos. 44, 46.

Centropistris atrarius, Günther; *Serranus atrarius*, Jor. and Gil. Sea bass; Black fish; Black sea bass. No. 251.

Epinephelus morio; Serranus morio, Günther. Grouper; Red grouper. Nos. 114, 271.

Lutjanus blackfordi. Red snapper. Nos. 20, 26, 242.

Diplodus argyrops; Pagrus argyrops, Günther. Porgy; Porgee; Scup; Scuppaug. Nos. 15, 31, 262.

Diplodus probatocephalus; Sargus ovis, Günther. Sheepshead; Ger., Schafbrassen. Nos. 48, 250.

Sciæna ocellata. Red bass; Channel bass; Red horse. No. 270.

Menticirrus nebulosus; Umbrina nebulosa, Günther. King fish; Whiting; Barb. No. 252.

Cynoscion regale; Otolithus regalis, Günther. Weak fish; Squeteague; Gray trout. No. 273.

Tautoga onitis. Black fish; Tautog; Oyster fish. Nos. 38, 205, 244, 269.

Phycis chuss; P. americanus, Günther. Hake; Codling; Squirrel hake. No. 113.

Brosmius brosme. Cusk. No. 110.

Gadus aeglefinus. Haddock; Fr., L'anon; Ger., Schellfisch. Nos. 16, 21, 229, 259.

Gadus morrhua. Common cod fish; Fr., Morue; Ger., Dorsch (young and fresh); Kabljau (old and fresh); Stockfisch (dried); Leberdan (salted). Nos. 3, 11, 25, 34, 37, 79, 80, 206, 228, 243.

Gadus tom-cod; G. tomcodus, Günther. Tom cod; Frost fish. No. 99.

Gadus virens. Pollock; Pollack; Coal fish; Green cod; Fr., Colin; Ger., Köhler. No. 81.

Hippoglosus vulgaris; Pleuronectes hippoglossus, Günther. Halibut; Fr., Fletan; Ger., Heilbutte. Nos. 1, 9, 211.

Platysomatichthys hippoglossoides; Hippoglossus groenlandicus, Günther. Turbot; Greenland halibut. No. 49.

Paralichthys dentatus; Pseudorhombus dentatus, Günther. Common flounder. Nos. 2, 22,

Pleuronectes americanus. Winter flounder; Mud dab. No. 253.

Petromyzon marinus. Lamprey eel; Sea lamprey; Fr., Lamproie; Ger., Seeneunange. No. 236.

Raia sp. Skate. No. 247. (Only part of specimen received for analysis, not sufficient to identify species.)

II.—METHODS OF ANALYSIS.

The methods employed for preparing the materials for analysis, and for the analytical determinations, have been referred to in the reports of the U. S. Fish Commission[1] above mentioned, and are to be discussed in full in the detailed report. It will therefore suffice to speak of them very briefly here.

Separation of flesh from refuse. Sampling.—The sample as received at the laboratory was weighed, the flesh (edible portion) separated from the refuse (bones, skin, entrails, spawn, etc.), and both portions weighed. There was always a slight loss in cleaning, due, evidently, to evaporation and to slimy and fatty matters and small fragments of the tissues that adhered to the hands and to the utensils used in preparing the sample. Perfect separation of the flesh from the other tissues was difficult, but the loss resulting from this was small, so that, though the figures obtained represent somewhat less than was actually in the sample, yet the amount thus wasted was doubtless scarcely more than would be left unconsumed at an ordinary table. The reasons for rejecting the skin, which generally has considerable nutritive value, were that its chemical constitution is different from that of the flesh, and that, so far as we have observed, it is not ordinarily eaten in this country. With the closer domestic economy that increased density of population must bring, people will doubtless become more careful hereafter to utilize such materials, and certainly a more accurate study of their chemical constitution is to be desired.

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[1] See also Ber. d. deutsch. chem. Gesell. **16**, 1883, s. 1839.

In sampling the material for analysis, it was finely chopped and well mixed in a wooden tray.

Water and water-free substance.—The drying was done in ordinary water-baths of large size, at a temperature of nominally 100°, but actually about 96° (as is, I believe, usual in such drying baths, which consist of an air chamber with double walls inclosing boiling water). In each case, one or more samples of 50 to 100 grams each of the freshly chopped flesh were weighed on a watch glass or small sauce plate, heated in a current of hydrogen for 24 to 48 hours, cooled, allowed to stand in the open air for some 24 hours, weighed, ground, sifted through a sieve with circular holes of 1 mm. diameter, bottled, and set aside for analysis. A few of the fattest samples, however, could not well be worked through so fine a sieve; for these, either a coarse sieve was used, or the substance was crushed as finely as practicable and bottled without sifting. For the complete drying, from 1 to 2 grams of the partly dried material were weighed in small drying flasks, and dried in hydrogen three or four hours. It is extremely difficult to get an absolutely constant weight, though we find that the object is in most cases approximately attained in three hours. The total moisture and water-free substance are computed from the two dryings.

The especial object in drying in hydrogen was to prevent possible oxidation of fats, whereby the latter would be rendered insoluble in ether, and the accuracy of their determination impaired. That this is at all necessary in animal tissues, or when it is necessary and when not, I am not prepared to affirm. But as a precaution in the early part of the work, we arranged an apparatus for drying in hydrogen,[1] and although the comparative trials in air and in hydrogen did not show any large differences in results, the apparatus was so convenient that we have used it throughout the investigation.

Drying in air.—As drying in air is nevertheless more convenient for large quantities, and suffices perfectly well for certain determinations, such as sulphur, phosphorus and chlorine, a sufficient quantity of material for this work was prepared by drying a portion in air. This was effected by weighing 200 grams or more of the freshly chopped substance at the same time that the portion was taken for drying in hydrogen, drying in the air-bath without hydrogen, exposing to air of room, weighing, grinding, and bottling as above.

Examination of the analytical details (in the detailed report) will show a number of cases in which the percentages of water-free substance in portions used for various determinations, nitrogen, fat, ash, etc., differ from those given in the water determination. This is due to the simple fact that some time intervened between the determinations, and that our experience showed that although reasonable care was used to procure bottles with well-fitting glass stoppers to hold the partly dried material, yet the moisture in the latter was liable to change on standing in the laboratory, and that both use of rubber stoppers and paraffine on the glass stoppers failed to prevent this so completely as to make us feel safe in using the substance after it had stood for more than a few days, without redetermination of the water.

Fats, Ether extract.—The fats were extracted with ether, which, after various trials with chloroform and benzine, we are persuaded is the most convenient solvent for the purpose.

The determinations were made in the material which had been nearly dried in hydrogen. Generally, from 0.3 to 1.0 gram was used for the extraction. The operation was conducted in an apparatus similar to that described by Johnson.[2] The corks and filter paper were always treated with ether before using. We have found it convenient, however, to duplicate the apparatus, using several at once. A rectangular box of zinc or galvanised iron, 70 or 80 cm. long, 17 cm. wide and 25 cm. high, and provided with six pipes of block tin which serve as worms, makes a very good cooler for the ether. We do not generally find it necessary to have a current of water running through the cooler, even in summer; the radiation of heat from the water is sufficient to keep it cool enough to condense the ether without being changed.

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[1] To be described elsewhere.

[2] Am. Jour. Sci. **13**, 1877, 190.

The point at which the extraction is completed we have not always found easy to determine. The methods ordinarily recommended, of evaporating a drop of the ether after it percolated through the substance, either on a piece of paper or on a clean watch glass, and noting whether a transparent spot or a residue remains, have not in our experience been satisfactory. We prefer to continue the extraction for such time as experience has indicated to be sufficient, and then remove the flask and substitute another, repeating this latter operation until the new flask shows no gain in weight after the extraction has been continued for some time. When the extraction is believed to be complete, the apparatus is taken off from the condensing tube, the inner tube holding the substance is taken out, a test tube substituted, the apparatus put back in place, and the ether in the flask is again warmed, allowed to condense and run back into the test tube and thus most conveniently recovered for subsequent use. The small portion of ether still adhering to the extract in the flask is removed by warming in a current of hydrogen in the apparatus used for drying.

The flasks are always weighed against a similar flask as counterpoise.

What other substances besides fats are thus extracted from the flesh of fish, oysters, etc., is a matter which I have not investigated, contenting myself for the present with simply calling the material extracted by ether, ether extract. As the analytical details show, the material used for fat determination was nearly dried in the hydrogen before extraction with ether. By this means two possible sources of error are avoided, to wit:

1. Certain fatty substances, as is well known, are rendered insoluble or very difficultly soluble in ether by being heated in air. This alteration, due, I suppose, to oxidation, is very marked in many vegetable substances. Thus I have found the larger part of the fats of linseed, maize, and grasses to be rendered insoluble in this way. Whether or to what extent any of the fats of the animal

Vol. 9
1887

tissues which we have analysed would be thus affected is a matter which I regret to have been unable thus far to study. That the error by drying in air would be large seems to me improbable.

2. When the material extracted contains considerable quantities of water, or when commercial ether containing water is used, other substances than fats may possibly be dissolved. When and how greatly the presence of water would affect the results I cannot tell, though I do not believe the error would be great in such substances as we are here dealing with.

The ether extract was nearly always more or less colored. In how far this was due to chemical or physical changes in the fats, and in how far to coloring matters extracted with them, I cannot say.

As regards the difficulty of extracting with ether, our experience shows that many of the vegetable fats, as those of maize, wheat, etc., are easily extracted, while those of animal tissues are often more difficult to get into solution. The fat, or, more properly, the materials soluble in ether, are more readily extracted from oysters, clams, lean beef, etc., than from the flesh of the fatter fish and the fatter meats. In general, the greater the percentage of fat in a substance the more difficult do we find the removal of the last traces. Mr. Woods remarks that "the flesh of eels was the hardest material to extract I have ever met." I should say that even the flesh of eel could hardly be much more difficult than the yolk of eggs, which, however, is of different composition. It is, I think, very important that the material to be extracted be fine, especially when it is hard and dry, as is often the case with partly dried flesh.

After the experience which we have had in extracting with ether, I am persuaded that correct results are far harder to obtain than is ordinarily believed. Indeed, I regard these determinations as among the more difficult ones with which we have had to do.

Nitrogen, protein, albuminoids, etc.—The nitrogen was determined in the partly dried substance by soda-lime. Several series of experiments were undertaken to get light upon the conditions under which correct determinations of nitrogen in animal tissues may be made by this method. Part of them have been,[1] and the others, it is hoped, will be, described in this Journal. We have come to believe that with proper precautions, extremely accurate determinations may be made with soda-lime, but that great care is needed to insure them.

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[1] Vol. 9, page 311.

It is customary to compute the albuminoids or protein (nitrogenous substances) by multiplying the nitrogen by 6.25. In our analyses this factor has, in general, been very nearly correct. I have thought it best, for the present purpose, to state the percentages of nitrogen and of protein as calculated by multiplying these by 6.25, and also to estimate the "albuminoids, etc." by difference. For the latter, the remainder left after subtracting the sum of ether extract and ash from the water-free substance, or the sum of water, ether extract and ash from the fresh substance, is used. This is, of course, not absolutely correct, but it is more nearly so than the product of nitrogen by 6.25 would be. This subject, however, demands special discussion.

Ash.—The ash was determined by carbonising a portion of the partly dried material, in the case of flesh preferably about 5 grams, extracting the charred mass with water, burning the residue, adding the solution, evaporating and burning. The charring and burning were conducted in platinum capsules over a gas flame. The crude ash thus obtained was practically free from coal. No determinations of carbonic acid were made.

Phosphorus.—A portion of the partly dried substance, preferably about one gram, was carefully burned in a platinum crucible with some ten grams of a mixture of equal parts of sodium nitrate and carbonate, previously proved free from phosphoric acid. The white mass was dissolved in water, acidulated with nitric acid, evaporated, and treated with nitric acid again, the operation being repeated when necessary to remove chlorine, and the phosphoric acid then estimated with ammonium molybdate solution.

A number of experiments were made to test the accuracy of the determinations in the presence of such large quantities of sodium nitrate, etc., as are necessarily used. Awaiting their publication in detail, it will suffice here to give the outcome, which was briefly this:

At the temperature of the trials, which was in each case not far from 29° C., two precautions are necessary: (1) the use of a large excess of the molybdate solution (unless nitric acid alone should perform the same office), and (2) allowance of ample time for precipitation. Neglect of these precautions involves risk of loss of phosphoric acid. The effect of higher temperature was not tested. Practically, we have used 25 cc. of molybdate solution and allow from 36 to 48 hours for the precipitation.

Sulphur.—About one gram of the nearly dried substance was oxidised as for the determination of phosphorus. The cooled mass was dissolved in hydrochloric acid, and the sulphuric acid determined by precipitation with barium chloride.

It is well known that the presence of salts of the alkalies, including sodium chloride, when present in considerable quantities, may affect the precipitation of sulphuric acid by barium chloride, the precipitate of barium sulphate bringing down with it under some circumstances more or less of the alkaline salt. The ordinary means for avoiding this consist in diluting the solution, precipitating hot, and washing the precipitate with hot water. In view of the large quantity of sodium chloride present in these determinations, it seemed desirable to study the conditions under which pure and impure barium sulphate precipitates are formed, a little more closely than had, so far as I am aware, been done. For this purpose a series of experiments were devised.

The plan consisted in taking a solution of sulphuric acid and determining the amount of acid both in the solution alone and after adding different quantities of sodium chloride. Comparative trials were made with concentrated and dilute solutions and by precipitating hot and cold. The sulphuric acid solution used was the same as employed for nitrogen determination with the soda lime. The sodium chloride solution contained about 25 per cent. of sodium chloride, and the barium chloride solution about 20 per cent. of the ordinary crystallised salt. Without going into details of the experiments, which will, I trust, be given later, it will suffice to say that, although when precipitated cold from concentrated solutions, the barium sulphate is apt to be too heavy, i. e. to bring down sodium chloride; yet, when precipitated hot, or even precipitated cold from dilute solutions, it was uniformly pure. This is in accordance with the previous observations on which general practice is based. Our determinations served simply to show the limits of concentration and amount of sodium chloride within which it is safe to work. It should be noted, however, that the solutions contained in all cases a small, but only a small, amount of free hydrochloric acid, and that only a small excess of barium chloride was used in the precipitation. Practically, the ordinary way as recommended by Fresenius is accurate for these determinations, even in presence of large amounts of sodium chloride, provided the proper precautions are observed. The experiments satisfied us that the presence of the sodium chloride in the determinations of sulphur, as we conducted them, did not interfere with the accuracy of the results.

Chlorine was determined by burning the partly dried substance in platinum evaporating dishes, as in the determinations of phosphorus and sulphur, and estimating the chlorine in the fused mass with ammonium sulphocyanide by Volhard's process.[1] Dr. Long, by whom the determinations were made, carried out, at my request, a series of experiments which led to the observance of certain precautions, and showed that with them very satisfactory results may be obtained in the determination of chlorine in such substances as those we were working with. The details of Dr. Long's experiments are reserved for publication with the experiments on phosphorus and sulphur above mentioned. The precautions are contained in the following statement of the method followed in the determinations of chlorine in fish flesh.

1. The substance was very slowly fused with a mixture of potassium nitrate and sodium carbonate so as to avoid any possible loss by spirting. It was observed that when the platinum capsule, in which the ignition was carried on, was covered with a watch glass, small portions of the substance were thrown out against it unless the operation was conducted very slowly. With care, however, there was no considerable loss, as indicated by either the appearance of the watch glass or actual determinations with sugar and a known amount of chlorine.

2. The fused mass was dissolved in chemically pure nitric acid, which was made quite dilute, since by using a stronger acid some chlorine could easily be driven off, as was found by experiment.

3. To the solution thus obtained an excess of silver nitrate solution (decinormal or half decinormal) was added, and the whole boiled on the water-bath for about two hours. This long boiling with excess of nitric acid, added after the silver nitrate, was found necessary to expel nitrous acid coming from the reduction of the nitrate in the fusion.

4. After the boiling, the solution was allowed to become quite cold before titrating.

Proximate ingredients directly determined.—In a number of the specimens, determinations were made of the ingredients soluble in cold and hot water, and of the portion not dissolved by water, alcohol, or ether. The object was as much to test the methods commonly employed as to learn the amounts of the ingredients. The methods have proved unsatisfactory in many respects, and we have felt it advisable to make no more determinations by them than are indicated in the tables, until the subject is worked up more thoroughly. For that matter, an at all satisfactory examination of the proximate constituents will involve the study of a good deal more than the compounds of the flesh. Considering the complicated character of the compounds concerned, the vagueness of our present knowledge of them, and the amount of preliminary work that is always necessary before such an investigation can be got into good running order; and adding to all this the importance of studying the elementary composition of the organic compounds, the mineral ingredients as well, it is clear that much labor will be necessary to reach the desired results. Those we have obtained will at least serve to compare with similar ones obtained by other analysts.[1]

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[1] Liebig's Annalen **190**, 1.

Cold-water extract.—Of the freshly chopped substance, 33⅓ grams were digested for eighteen to twenty-four, generally about twenty, hours in 500 cc. of cold water, and filtered. The filtration was conducted at first through "coffee filter paper," but we have found it better to use fine linen cloth, which has the advantages of more rapid filtration and of allowing the liquid to be squeezed through with proper care. The solids do not pass through the cloth more than through the filter paper, and by laying on a glass plate, scraping, and subsequent rinsing, they are separated much more easily and completely than they can be from the filter paper.

Albumen coagulated from cold-water extract.—The filtrate thus obtained was boiled and filtered through previously dried and weighed asbestos filters. After washing with ether, the filter with its contents was dried and weighed. That this method for determining albumen is accurate is by no means proven or even probable. Indeed, in some species of fish at least—and the same is true of other animals—the cold-water extract of the muscular tissues contains a form of albumen, or at any rate a substance or substances closely resembling albumen, which is not precipitated by boiling at all, except after the addition of large quantities of acid or salts. When the determinations in question were made, this substance had not been well studied, but I was persuaded that the method followed was not reliable for the determination of the actual amount of albumen, a view which studies to be elsewhere discussed have amply confirmed.

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[1] See Almén, *Analyse des Fleisches einiger Fische*, Nova Acta Reg. Soc. Sc. Ups., Ser. III, Upsala, 1877.

Extractive matters. Cold-water extract not coagulated by boiling.—The filtrate from the coagulated albumen was evaporated in platinum capsules and weighed. One portion was used for determination of the ash, which was done by charring at a low temperature, extracting with water, igniting the residue until it was well burned, adding the water solution, evaporating, igniting carefully at a low temperature, and weighing. The other portion was finely ground, dried in air to determine the percentage of water, and extracted with ether until free from fat, usually two or three hours. The crude extract, minus the water, fat, and ash, is reckoned as pure extract, and is designated as "extractive matters." It of course contains the albumen which was not coagulated, the other nitrogenous compounds, the carbohydrates, and whatever else, except fats and mineral matters, was taken from the flesh of the fish by the digestion in cold distilled water.

Hot-water extract. "Gelatin."—The residue left after the extraction with cold water was treated for 18 to 24 hours, generally about 20 hours, with distilled water at 100° or slightly below. It was then filtered through weighed asbestos filters, and the filtrate evaporated to dryness in platinum, and weighed as "crude gelatin." In this fat and ash were determined, and the pure extract, called in the tables "gelatin," estimated as in the cold-water extract. It should be stated that in both hot and cold water extracts, the figures for total extract in the tables represent water-free substance, i. e. crude extract minus water. I am inclined to think it would be better to determine both water and fat in the crude extracts in one operation by extracting with ether and noting the loss.

Insoluble protein.—The residue left after the extraction with hot water was treated with alcohol or ether, or both, dried and weighed. Water, ash, and fat were then determined (except, of course, that fat was not determined in the cases where it had been previously extracted). The ash was determined by direct burning, it being assumed that the previous treatment with cold and hot water had sufficed to remove the easily fusible and volatile salts. The removal of the last portions of fat is often extremely difficult, and it is not impossible that in some cases traces were left and weighed as insoluble protein. The figures for total insoluble protein in the tables denote water-free substance.

It is perhaps superfluous to state that the determinations were all made in duplicate. The figures given in the tables which follow represent the averages of the closely agreeing results. The analytical details are to be given in full in the monograph mentioned above.

III.—Tabular Statements of Analyses.

Tables I to X recapitulate the results of the analyses of American fishes.

Table I gives the localities of the specimens as stated by the parties from whom they were received, the portions received for analysis, results of weighings in preparing for analysis, etc. The "loss in preparing for analysis" I suppose to have consisted chiefly of water which evaporated during the process, and of material which adhered to the hands and the instruments with which the separations were made. The specimens are here put, for convenience, in numerical order. The full report referred to will contain further descriptions and details regarding these specimens, and will give similar data for preserved fish, which are omitted from the present condensed account.

Table II gives results of analyses of flesh calculated on water-free substance. It will be observed that the percentages of protein as estimated by multiplying the nitrogen by the factor 6.25, and those of "albuminoids, etc." (actual nitrogenous substances) as estimated by difference [100—(ether extract + ash) = albuminoids, etc.], are both given. The former (protein = N × 6.25) has the sanction of common usage, but the latter comes nearer to the truth. We certainly cannot go far away in assuming that the flesh of fish contains ordinarily but very little of non-nitrogenous compounds other than fats and mineral compounds, though a more thorough study of the carbohydrates and complex nitrogenous and phosphorised fats is much needed. Accordingly it seems to me that in these analyses the most accurate measure of the nitrogenous compounds is to be found by subtracting the sum of the ether extract and ash from the whole.

Table III gives analyses of flesh calculated on fresh substance, and includes both protein as estimated by multiplying N by 6.25, and "albuminoids, etc.," by difference [100 — (water + ether extract + ash) = albuminoids, etc.] The figures of this table are computed from those of Table II, the percentages of water and water-free substance in the flesh and of ingredients in water-free substance serving as the basis of the calculations. In the subsequent tables, deduced from these and taken as representing the actual composition of the flesh, the latter figures rather than those obtained by multiplying N by 6.25 are taken as representing the nitrogenous matters.

It will be interesting to observe the differences between results obtained by estimating the nitrogenous substance in this way (see section on "Nitrogen, Protein, etc." in chapter on Methods of Analysis, above) and by multiplying the percentage of nitrogen by the factor 6.25. The figures of Table IV give the sum of protein (N × 6.25), ether extract, and ash in the water-free substance, and of these and water in the flesh, both of the specimens in Tables II and III and of those of "prepared fish" in Tables VIII and IX beyond. If we leave the carbohydrates out of account, assume the ash to represent the mineral matters, and take ether extract as representing the fats, but as including no nitrogenised fats, then the figures for "albuminoids, etc., by difference" will represent exactly the amount of nitrogenous substance (albuminoids, gelatinoids, nitrogenous extractives, and nitrogenised fats). Of course, these assumptions are not absolutely correct. The flesh contains a minute quantity of carbohydrates (including all non-nitrogenous substances other than fats); the ash is not the exact measure of the mineral matters, and the ether extract does not exactly represent the neutral fats. But the errors involved are small, and until better methods of analysis are devised and brought into current use, "albuminoids, etc., by difference" will be the closest approach to the actual nitrogenous substance.

The current method of estimating the nitrogenous material is by multiplying the nitrogen by 6.25. To this product, various terms, as albuminoids, proteids and protein, are applied. If the figures for "albuminoids, etc., by difference" were the exact measure of the nitrogenous substance, the difference between them and the product of N × 6.25 would be the error in computing protein in this latter way. In Table II, the ash + ether extract + "albuminoids by difference" = 100, and the ash + ether extract + protein (N × 6.25) =

a quantity varying more or less from 100. On the assumption that the "albuminoids by difference" represent the actual nitrogenous substance, the variations from 100 in the latter figures represent the error in calculating protein by multiplying N by 6.25.

Of course, the correct determination of actual nitrogenous substance involves numerous other questions in addition to those here suggested, and first of all, the chemical and physiological distinctions between the different nitrogenous compounds. But for the present purpose it will suffice to take the "albuminoids, etc., by difference" as the measure of the nitrogenous material.

Table IV gives the sum of ash + fat + protein (N × 6.25) in water-free substance, and of water + ash + fat + protein (N × 6.25) in flesh, of the specimens of fish in Tables II and III, and of prepared fish in Tables VIII and IX beyond. For the water-free substance the range of the figures is from 97.01 to 116.01, but in the flesh (leaving the preserved fish out of account) the range is only from 99.34 to 102.85, or, omitting the skate, to 101.14. The only cases in which the sum is below 99 in the water-free substance of the fresh flesh are those of the spent salmon. In these, both nitrogenous substance and fat had been reduced during the spawning season. The only ones above 101 in the flesh are two specimens of fat salmon, one each of sea bass and turbot, several of cod, and one of skate. It is clear that the use of either the figures for protein, N × 6.25, or "albuminoids, etc., by difference" for the total nitrogenous substance in the flesh, will involve no very serious error except in the last named cases.

The figures for protein in sea bass, turbot, cod, and especially skate, are a little surprising. The question naturally suggests itself whether there may not be errors in the analyses. I think the analytical details, when published, will show that this explanation is extremely improbable. All the nitrogen determinations in the specimens of cod gave large figures. Two determinations in the specimens of skate gave respectively 16.28 and 16.29 per cent. in the water-free substance. These figures are so large that a third determination was made, with 16.30 as the result.

In brief, while the error involved in estimating the total nitrogenous substance by multiplying the nitrogen by the factor 6.25 in the usual way, is, when viewed from the exact scientific standpoint, very considerable in many cases, it is seldom large enough to be of great practical importance. The exceptional cases, however, demand further study.

TABLE I.

List of Specimens of American Fishes Analyzed, Names, Localities, and Proportions of Flesh, etc.

KINDS OF FISH, LOCALITIES, AND PORTION TAKEN FOR ANALYSIS.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Proportion of Flesh, etc., in Specimen as taken for Analysis.					
				Total Weight of Specimen			Flesh, Edible Portion.	Refuse, Bones, Skin, Entrails, etc.	Loss in Preparation for Analysis.
				lbs.	oz.	grams.	per ct.	per ct.	per ct.
Halibut, posterior part of body, lean	1	Spring.	...	4	2.7	1894.0	75.92	23.12	0.96
Common flounder, entrails removed	2	"	2	5	1.2	2308.0	41.33	57.02	1.65
Cod, head and entrails removed	3	"	1	6	1.9	2780.0	69.57	23.70	1.73
Eel (salt water), skin, head and entrails removed	4	"	11	3	0.1	1368.0	76.24	21.42	2.34
Alewife, whole, Connecticut River	5	"	12	1	14.2	859.0	49.48	50.52	...
Shad, whole, Hudson River, first of season	6	"	2	4	3.8	1925.0	48.31	49.35	2.34
Striped bass, whole, Connecticut River	7	"	1	4	8.4	2055.0	42.09	56.69	1.22
Mackerel, whole	8	"	4	2	13.0	1280.0	60.55	38.28	1.17
Halibut, section of body, fatter than No. 1	9	"	...	2	6.0	1075.0	88.28	11.16	0.56
Shad, whole, Connecticut River, early in season	10	"	1	3	8.2	1595.0	52.35	46.40	1.25
Cod, head and entrails removed	11	"	1	5	9.2	2532.0	68.13	30.57	1.30
Blue fish, entrails removed	12	"	1	3	1.3	1400.0	50.14	48.57	1.29
Mackerel, whole	13	"	2	1	15.7	898.2	45.76	51.77	2.47
Salmon, entrails removed, Maine	14	"	1	10	8.0	4764.3	76.16	23.84	...
Porgy, whole	15	"	4	2	9.9	1190.5	33.16	65.17	1.67
Haddock, entrails removed	16	"	1	4	2.9	1900.0	46.84	51.42	1.74
Lake trout (Mackinaw trout), whole, Lake Ontario	17	November.	1	7	14.8	3600.4	43.31	56.32	0.37
White fish, whole, Lake Champlain	18	"	1	2	14.3	1313.0	45.76	53.47	0.77
Striped bass, whole, Bridgehampton, Long Island	19	"	1	2	6.7	1098.5	42.51	56.90	0.59
Red snapper, whole, Fernandina, Florida	20	"	1	7	11.7	3507.5	60.00	39.60	0.40
Haddock, entrails removed, Rockaway, Long Island	21	"	1	5	4.7	2402.0	47.50	51.62	0.88
Common flounder, whole, Amagansett, Long Island	22	March.	1	2	12.3	1257.5	31.97	66.80	1.23
Smelt, whole, Hackensack River, New Jersey	23	"	73	2	4.0	1023.0	61.78	34.82	3.40
Brook trout, whole, cultivated, Long Island	24	"	6	2	13.6	1295.0	46.95	50.11	2.94
Red snapper, entrails removed, Florida, East coast	26	April.	1	12	1.6	5498.7	47.36	52.45	0.19

TABLE I.—*Continued.*

KINDS OF FISH, LOCALITIES, AND PORTION TAKEN FOR ANALYSIS.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Proportion of Flesh, etc., in Specimen as taken for Analysis.					
				Total Weight of Specimen.			Flesh, Edible Portion.	Refuse, Bones, Skin, Entrails, etc.	Loss in Preparation for Analysis.
				lbs.	oz.	grams.	per ct.	per ct.	per ct.
Mackerel, whole, Cape May, New Jersey	30	May.	4	5	11.3	2594.0	50.29	48.85	0.86
Porgy, whole, Rhode Island	31	"	4	6	4.6	2857.0	41.65	57.33	1.02
Shad, whole, Connecticut River	32	"	1	3	13.7	1752.0	52.80	45.89	1.31
Black fish, whole, Stonington, Connecticut	38	December.	2	4	8.6	2060.0	42.16	56.15	1.69
Mackerel, whole, Cape Cod, Massachusetts	39	"	1	1	2.4	522.1	64.60	33.78	1.62
Spanish mackerel, whole	43	March.	1	3	5.2	1512.4	64.02	34.61	1.37
White perch, whole	44	"	2	1	11.1	770.1	35.24	63.24	1.52
Mascalonge, whole, St. Lawrence River	45	"	1	9	1.0	4118.0	50.57	49.23	0.20
White perch, whole	46	"	4	2	0.9	935.9	36.24	61.80	1.96
Herring, whole	47	"	4	2	6.0	1080.8	51.13	46.00	2.87
Sheepshead, entrails removed, Florida	48	"	1	4	5.5	1974.2	42.07	56.59	1.34
Turbot, or Greenland halibut, whole, Newfoundland	49	"	1	5	8.0	2496.5	52.27	46.04	1.69
Pike perch, or Wall-eyed pike, whole	52	"	2	2	7.5	1122.7	41.21	57.25	1.54
Large-mouthed black bass, whole, North Carolina	53	"	1	3	11.1	1676.5	43.16	56.05	0.79
Salmon (female), whole, Penobscot River	77	July.	1	13	1.8	5948.0	66.54	32.98	0.48
Salmon (female), whole, Penobscot River	78	"	1	11	3.3	5082.0	69.22	30.58	0.22
Pollock, head and entrails removed, Massachusetts coast	81	October.	1	5	13.1	2638.0	69.64	28.50	1.86
Butter fish, whole, east end of Long Island	90	November.	4	1	9.6	724.0	55.86	42.76	1.38
Small-mouthed black bass, whole, Seneca Lake, N. Y.	91	"	2	1	11.2	772.8	45.36	53.66	0.98
Pike, entrails removed, Lake Ontario	98	"	1	3	9.0	1617.0	55.69	42.67	1.64
Tom-cod, whole, south side of Long Island	99	"	4	2	7.6	1131.6	39.06	59.88	1.06
Pickerel, whole, Seneca Lake, New York	100	"	3	2	2.5	960.6	53.14	45.44	1.42
Cusk, entrails removed, Massachusetts coast	110	December.	1	3	2.7	1436.5	58.40	40.28	1.32
Cisco, whole, Lake Erie	111	"	4	2	12.4	1256.0	55.95	42.70	1.35
Hake, entrails removed, off Coney Island, New York	113	"	1	14	6.5	6534.5	47.54	52.46	...
Grouper (Red grouper), entrails removed, Pensacola, Florida	114	"	1	3	7.0	1559.0	43.55	55.77	0.68
Mullet, whole, Virginia	126	"	1	1	8.9	707.5	40.99	57.88	1.13
Yellow perch, whole, Lake Champlain	127	"	4	2	8.8	1152.0	36.56	62.64	0.80

TABLE I.—*Continued.*

Kinds of Fish, Localities, and Portion Taken for Analysis.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Proportion of Flesh, etc., in Specimen as taken for Analysis.					
				Total Weight of Specimen.			Flesh, Edible Portion.	Refuse, Bones, Skin, Entrails, etc.	Loss in Preparation for Analysis.
				lbs.	oz.	grams.	per ct.	per ct.	per ct
Black fish, whole	205	March.	1	3	3.0	1446.5	33.95	64.08	1.97
Cod (Rock cod), whole, near Block Island	206	"	1	4	2.3	1881.0	42.85	56.51	0.64
Smelt, whole, Maine coast	207	"	14	0	14.0	398.0	47.99	48.99	3.02
Yellow perch, head, entrails, fins and tail removed, Connecticut River	208	"	6	0	10.7	302.0	60.60	35.10	4.30
Halibut, sections of different parts of body, George's Banks.	211	"	...	8	2.7	3705.0	79.52	18.70	1.78
Shad, whole, Delaware River	212	"	1	2	10.2	1196.0	53.77	44.39	1.84
Eel (salt water), head, skin and entrails removed, north coast Long Island.	217	April.	6	0	15.4	436.0	76.14	19.04	4.82
Alewife, whole, Connecticut River	220	"	4	1	14.8	879.2	47.90	49.42	2.68
Shad, whole, Connecticut River	221	"	1	3	3.5	1461.0	45.18	53.25	1.57
Pickerel, whole, Connecticut River	224	"	2	1	5.2	600.0	48.16	48.67	3.17
Striped bass, whole, Long Island Sound	225	"	1	2	7.9	1132.0	49.63	48.59	1.78
Cod, head and entrails removed	228	"	1	7	7.4	3387.0	72.90	25.54	1.56
Haddock, entrails removed.	229	"	1	3	4.2	1480.0	49.73	47.97	2.30
Mackerel, entrails removed	230	"	2	1	6.6	640.0	57.35	40.65	2.00
California salmon, section of anterior part of body	233	"	...	1	14.7	870.5	88.70	10.34	0.96
Pompano, whole, Pensacola, Florida	234	"	1	1	8.1	683.5	56.24	42.37	1.39
Lamprey eel, whole, Hackensack River	236	"	2	2	13.6	1295.0	50.40	45.79	3.81
Striped bass, whole, North Carolina	237	"	1	2	12.8	1270.0	41.37	57.08	1.55
Sturgeon, section of anterior part of body, Delaware River	238	"	...	1	10.6	753.0	84.72	14.41	0.87
Red snapper, entrails and gills removed, Pensacola, Florida	242	"	1	4	1.2	1848.0	54.33	45.29	0.38
Cod, whole, Long Island	243	"	1	5	7.5	2481.0	49.78	48.53	1.69
Black fish, entrails removed, Massachusetts	244	"	1	2	8.5	1147.0	40.80	57.81	1.39
Shad, whole, Hudson River	245	"	1	3	7.7	1579.0	45.92	52.69	1.39
Skate, left lobe of body	247	"	...	4	11.9	2150.0	46.32	51.03	2.65
Striped bass, whole, Long Island	248	"	1	2	0.0	906.0	42.93	55.41	1.66
Shad, whole, North Carolina	249	"	1	3	15.6	1801.0	39.75	58.75	1.50
Sheepshead, whole, North Carolina	250	"	1	1	15.3	886.5	32.61	65.98	1.41
Sea bass, whole, Pensacola, Florida	251	"	1	6	9.3	2985.0	43.84	56.09	0.07

TABLE I.—*Concluded.*

KINDS OF FISH, LOCALITIES, AND PORTION TAKEN FOR ANALYSIS.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Proportion of Flesh, etc., in Specimen as Taken for Analysis.					
				Total Weight of Specimen.			Flesh, Edible Portion.	Refuse, Bones, Skin, Entrails, etc.	Loss in Preparation for Analysis.
				lbs.	oz.	grams.	per ct.	per ct.	per ct.
King fish, whole, North Carolina	252	April.	1	1	8.2	685.5	42.16	56.60	1.24
Winter flounder, whole, Rhode Island coast	253	"	1	1	10.5	751.0	41.16	56.20	2.64
Brook trout, whole, cultivated, Long Island	254	"	3	0	12.3	353.1	51.15	45.20	3.65
Lake trout (Mackinaw trout), entrails removed, Lake Ontario	255	"	1	5	7.4	2477.0	63.58	35.21	1.21
Brook trout, whole, Montreal, Canada	256	"	1	0	12.2	346.0	48.86	49.12	2.02
Pike perch, or Gray pike, whole, Cleveland, Ohio	257	"	1	0	12.3	349.5	35.20	63.23	1.57
Small-mouthed red horse, entrails removed, Cleveland, Ohio	258	"	1	3	5.0	1500.0	46.20	52.47	1.33
Coast haddock, entrails removed, Long Island	259	"	1	7	2.1	3235.0	46.09	52.89	1.02
Striped bass, entrails removed, Long Island coast	260	"	1	2	2 2	969.5	47.96	51.16	0.88
Mackerel, whole, Virginia Capes	261	"	1	1	4.4	576.0	48.43	50.35	1.22
Porgy, whole, Gravesend Bay, Long Island	262	"	1	1	15.6	896.0	41.70	57.58	0.72
Pompano, whole, Pensacola, Florida	263	"	1	2	1.5	949.0	50.39	48.56	1.05
Black fish, entrails removed, Rhode Island	269	May.	1	2	10.0	1189.0	45.30	53.57	1.13
Red bass, whole, North Carolina	270	"	1	6	11.1	3033.0	36.47	63.53	...
Red grouper, entrails removed, Pensacola, Florida	271	"	1	11	12.5	5344.0	44.05	55.95	...
Weak fish, whole, Long Island	273	"	2	2	0.0	909.4	47.01	51.89	1.10
Salmon (female), whole, Penobscot River, Maine	279	June.	1	11	3.5	5107.0	64.27	35.73	...
Salmon (male), whole, Penobscot River, Maine	280	"	1	12	10.0	5826.0	60.45	39.55	...
ROE.									
Shad roe, from shad No. 245	246	April.	...	0	9.0	257.0	100.00	...	...
SPENT FISH.									
Salmon (male), whole, Penobscot River, Maine	35	November.	2	18	11.3	8482.7	55.72	43.78	0.50
Salmon (female), whole, Penobscot River, Maine	36	"	2	22	8.0	10204.9	56.18	43.54	0.27
Land-locked salmon (male), whole, Grand Lake Stream, Maine	40	December.	4	12	8.6	5686.3	50.74	48.41	0.85
Land-locked salmon (female), whole, Grand Lake Stream, Maine	41	"	4	7	15.8	3622.3	52.50	46.20	1.30

TABLE II.

Composition of Water-free Substance of Flesh of American Fishes.

NAMES OF FISH.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25.	Fats. Ether Extract.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Sturgeon	238	13.63	85.19	8.90	6.72	100.81	84.38
Small-mouthed red horse	258	13.43	83.94	10.98	5.56	100.48	83.46
Herring	47	9.87	61.69	35.55	4.83	102.07	59.62
Alewife	5	12.61	78.81	15.88	6.08	100.77	78.04
"	220	11.67	72.94	22.28	5.48	100.70	72.24
" Average of 2 specimens	...	12.14	75.87	19.08	5.78	100.73	75.14
Shad	6	9.83	61.44	35.67	4.26	101.37	60.07
"	10	9.19	57.38	39.10	4.26	100.74	56.64
"	32	9.90	61.88	34.50	4.58	100.96	60.92
"	212	10.06	62.87	35.32	3.09	101.28	61.69
"	221	11.48	71.75	23.24	5.46	100.45	71.30
"	245	10.57	66.06	29.10	5.52	100.68	65.38
"	249	11.06	69.13	26.58	5.16	100.87	68.26
" Average of 7 specimens	...	10.30	64.36	31.93	4.62	100.91	63.47
Smelt	23	13.32	83.25	9.76	10.08	103.09	80.16
"	207	13.66	85.38	7.55	6.24	99.17	86.21
" Average of 2 specimens	...	13.49	84.31	8.65	8.16	101.13	83.19
White fish	18	12.16	76.00	21.51	5.36	102.87	73.13
Cisco	111	12.92	80.75	14.59	5.25	100.59	80.16
California salmon	27	...	......	51.59	2.98	......	45.43
" "	233	8.37	52.31	46.51	2.85	101.67	50.64
" " Average of 2 specimens	...	...	......	49.05	2.92	.....	48.03
Salmon	14	9.57	59.81	37.94	3.35	101.10	58.71
" Female	77	9.47	59.19	40.98	4.26	104.43	54.76
" "	78	9.71	60.69	38.20	4.19	103.08	57.61
" "	279	10.24	64.00	33.76	3.51	101.27	62.73
" Male	280	10.17	63.56	33.53	3.73	100.82	62.74
" Average of 5 specimens	...	9.83	61.45	36.88	3.81	102.14	59.31
Spent salmon. Male	35	12.39	77.44	17.66	4.51	99.61	77.83
" " Female	36	12.93	80.81	12.98	5.36	99.15	81.66
" " Average of 2 specimens	...	12.66	79.13	15.32	4.93	99.38	79.75

TABLE II.—*Continued.*

NAMES OF FISH.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25.	Fats, Ether Extract.	Ash.	Protein + Fats + Ash.	Albumino ds, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Spent land-locked salmon. Male	40	11.70	73.13	18.12	5.76	97.01	76.12
“ “ “ “ Female	41	13.26	82.88	9.36	5.76	98.00	84.88
“ “ “ “ Average of 2 specimens	...	12.48	78.00	13.74	5.76	97.50	80.50
Lake trout	17	9.04	56.50	40.14	4.33	100.97	55.53
“	255	10.19	63.69	33.47	3.85	101.01	62.68
“ Average of 2 specimens	...	9.62	60.10	36.80	4.09	100.99	59.11
Brook trout	24	13.25	82.81	11.61	6.33	100.75	82.06
“	254	14.92	93.25	3.72	4.75	101.72	91.53
“	256	13.41	83.81	12.14	5.08	101.03	82.78
“ Average of 3 specimens	...	13.86	86.62	9.16	5.39	101.17	85.46
Pickerel	100	14.63	91.43	2.58	6.14	100.15	91.28
“	224	14.86	92.88	2.38	5.46	100.72	92.16
“ Average of 2 specimens	...	14.74	92.15	2.48	5.80	100.43	91.72
Pike	98	14.78	92.38	2.87	5.07	100.32	92.06
Mascalonge	45	13.58	84.87	10.70	6.63	102.20	82.67
Eel, salt water	4	10.20	63.75	34.23	3.04	101.02	62.73
“ “	217	10.68	66.75	29.62	4.16	100.53	66.22
“ “ Average of 2 specimens	...	10.44	65.25	31.92	3.60	100.77	64.48
Mullet	126	12.40	77.50	18.45	4.66	100.61	76.89
Mackerel	8	13.72	85.75	10.31	4.67	100.73	85.02
“	13	10.89	68.06	27.26	4.83	100.15	67.91
“	30	11.25	70.31	27.04	5.02	102.37	67.94
“	39	8.48	53.00	45.28	4.11	102.39	50.61
“	230	11.85	74.06	22.28	4.60	100.94	73.12
“	261	12.66	79.10	17.13	5.23	101.46	77.64
“ Average of 6 specimens	...	11.47	71.71	24.88	4.75	101.34	70.38
Spanish mackerel	43	10.76	67.25	29.56	4.71	101.52	65.73
Pompano	234	9.00	56.25	41.40	2.95	100.60	55.65
“	263	14.16	88.50	7.51	4.69	100.70	87.80
“ Average of 2 specimens	...	11.58	72.37	24.46	3.82	100.65	71.72
Blue fish	12	14.42	90.13	5.79	5.91	101.83	88.30
Butter fish	90	9.60	60.00	36.80	3.82	100.62	59.38
Large-mouthed black bass	53	14.54	90.88	4.47	5.57	100.92	89.96

TABLE II.—*Continued.*

NAMES OF FISH.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25.	Fats. Ether Extract.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Small-mouthed black bass	91	13.79	86.19	9.69	4.93	100.81	85.38
Yellow perch	127	14.54	90.88	2.81	5.86	99.55	91.33
“ “	208	14.37	89.81	5.11	6.12	101.04	88.77
“ “ Average of 2 specimens	...	14.46	90.34	3.96	5.99	100.29	90.05
Pike perch, Wall-eyed pike	52	14.67	91.69	2.31	6.75	100.75	90.94
Pike perch, Gray pike	257	14.94	93.38	3.95	5.90	103.23	90.15
Striped bass	7	14.25	89.05	7.47	5.51	102.03	87.02
“ “	19	13.40	83.78	10.49	6.69	100.96	82.82
“ “	225	13.36	83.50	12.35	4.92	100.77	82.73
“ “	237	12.90	80.63	15.02	5.23	100.88	79.75
“ “	248	13.72	85.75	9.93	5.05	100.73	85.02
“ “	260	12.32	77.00	19.75	3.92	100.67	76.33
“ “ Average of 6 specimens	...	13.32	83.28	12.50	5.22	101.00	82.28
White perch	44	11.79	73.69	23.07	4.56	101.32	72.37
“ “	46	13.59	84.94	10.42	5.27	100.63	84.31
“ “ Average of 2 specimens	...	12.69	79.31	16.74	4.92	100.97	78.34
Sea bass	251	15.34	95.88	2.36	6.80	105.04	90.84
Grouper	114	14.88	93.00	2.39	5.79	101.18	91.82
“	271	15.06	94.13	3.39	5.42	102.94	91.19
“ Average of 2 specimens.	...	14.97	93.57	2.89	5.60	102.06	91.51
Red snapper	20	14.82	92.63	2.85	5.82	101.30	91.33
“ “	26	13.96	87.25	8.58	5.86	101.69	85.56
“ “	242	15.26	95.38	2.67	6.48	104.53	90.85
“ “ Average of 3 specimens	...	14.68	91.75	4.70	6.05	102.50	89.25
Porgy	15	13.74	85.88	7.18	6.88	99.94	85.94
“	31	10.77	67.31	28.04	4.81	100.16	67.15
“	262	11.65	72.81	22.54	5.22	100.57	72.24
“ Average of 3 specimens	...	12.05	75.33	19.25	5.64	100.22	75.11
Sheepshead	48	11.90	74.38	24.02	3.93	102.33	72.05
“	250	14.81	92.56	3.16	6.36	102.08	90.48
“ Average of 2 specimens	...	13.36	83.47	13.59	5.14	102.20	81.27
Red bass	270	14.65	91.56	2.89	6.67	101.12	90.44
King fish	252	14.57	91.08	4.53	5.68	101.29	89.79

TABLE II.—*Concluded.*

NAMES OF FISH.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25.	Fats. Ether Extract.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Weak fish	273	13.54	84.63	11.37	5.64	101.64	82.99
Black fish	38	13.42	83.88	12.20	5.54	101.62	82.26
“	205	15.12	94.52	2.95	3.48	100.95	93.57
“	244	14.86	92.88	3.05	5.05	100.98	91.90
“	269	14.07	87.94	6.69	6.30	100.93	87.01
“ Average of 4 specimens	...	14.37	89.81	6.22	5.09	101.12	88.69
Hake	113	14.56	91.00	3.97	5.77	100.74	90.26
Cusk	110	15.10	94.38	0.94	4.98	100.30	94.08
Haddock	16	15.08	94.25	0.85	5.82	100.92	93.33
“	21	14.77	92.31	0.78	8.72	101.81	90.50
“	229	14.97	93.56	1.82	6.78	102.16	91.40
“	259	15.27	95.44	1.93	5.71	103.08	92.36
“ Average of 4 specimens	...	15.02	93.89	1.34	6.76	101.99	91.90
Cod	3	15.00	93.75	1.66	7.62	103.03	90.72
“	11	15.50	96.88	2.39	7.60	106.87	90.01
“	206	15.20	95.00	1.54	7.22	103.76	91.24
“	228	15.30	95.63	1.89	6.03	103.55	92.08
“	243	15.10	94.38	2.89	6.95	104.22	90.16
“ Average of 5 specimens	..	15.22	95.13	2.07	7.08	104.28	90.84
Tom-cod	99	14.95	93.44	2.08	5.32	100.84	92.60
Pollock	81	14.41	90.06	3.23	6.45	99.74	90.32
Halibut	1	13.46	84.06	10.59	5.53	100.18	83.88
“	9	9.93	62.06	35.41	3.83	101.30	60.76
‘	211	13.67	85.43	11.95	3.81	101.19	84.24
“ Average of 3 specimens	...	12.35	77.18	19.32	4.39	100.89	76.29
Turbot	49	8.25	51.56	50.36	4.47	106.39	45.17
Common flounder	2	14.35	89.69	3.73	7.67	101.09	88.60
“ “	22	14.14	88.38	5.18	8.63	102.19	86.19
“ “ Average of 2 specimens	...	14.24	89.03	4.46	8.15	101.64	87.39
Winter flounder	253	14.86	92.88	2.85	7.68	103.41	89.47
Lamprey eel	236	8.30	51.88	46.03	2.27	100.18	51.70
Skate	247	16.29	101.82	7.81	6.3	116.01	85.81

TABLE III.

Composition of Flesh of American Fishes.

KIND OF FISH.	Laboratory Numbers of Specimens	Water.	Water-free Substance.	Albuminoids, etc. (by difference).	Fats. Ether Extract.	Ash.	Nitrogen.	Protein, N × 6.25.	Water + Protein + Fats + Ash.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Sturgeon	238	78.71	21.29	17.96	1.90	1.43	2.90	18.11	100.15
Small-mouthed red horse	258	78.56	21.44	17.90	2.35	1.19	2.88	17.99	100.09
Herring	47	69.03	30.97	18.46	11.01	1.50	3.06	19.12	100.66
Alewife	5	75.92	24.08	18.80	3.82	1.46	3.04	19.00	100.20
"	220	72.69	27.04	19.54	6.02	1.48	3.16	19.72	100.18
" Average of 2 specimens	...	74.44	25.56	19.17	4.92	1.47	3.10	19.36	100.19
Shad	6	69.65	30.35	18.25	10.80	1.30	2.98	18.64	100.39
"	10	65.25	34.75	19.68	13.59	1.48	3.18	19.89	100.21
"	32	70.75	29.25	17.83	10.08	1.34	2.89	18.08	100.25
"	212	71.04	28.96	17.83	10.23	0.90	2.92	18.19	100.36
"	221	71.98	28.02	19.98	6.51	1.53	3.21	20.10	100.12
"	245	72.14	27.86	18.24	8.08	1.54	2.95	18.40	100.16
"	249	73.56	26.44	18.05	7.03	1.36	2.92	18.27	100.22
" Average of 7 specimens	...	70.62	29.38	18.56	9.47	1.35	3.01	18.83	100.27
Smelt	23	80.16	19.84	15.90	1.94	2.00	2.64	16.52	100.62
"	207	78.16	21.84	18.83	1.65	1.36	2.98	18.65	99.82
" Average of 2 specimens	...	79.16	20.84	17.37	1.79	1.68	2.81	17.59	100.22
White fish	18	69.83	30.17	22.06	6.49	1.62	3.67	22.93	100.87
Cisco	111	76.15	23.85	19.12	3.48	1.25	3.08	19.26	100.14
California salmon	27	62.68	37.32	16.96	19.25	1.11	3.26	.....	.....
" "	233	64.53	35.47	17.96	16.50	1.01	2.97	18.56	100.60
" " Average of 2 specimens	...	63.61	36.39	17.46	17.87	1.06	3.12	.....	.....
Salmon	14	67.15	32.85	19.17	12.47	1.21	3.15	19.63	100.46
" Female	77	63.41	36.59	20.04	14.99	1.56	3.46	21.66	101.62
" "	78	65.08	34.92	20.12	13.34	1.46	3.39	21.19	101.07
" "	279	61.37	38.63	24.23	13.04	1.36	3.95	24.72	100.49
" Male	280	61.03	38.97	24.45	13.07	1.45	3.96	24.77	100.32
" Average of 5 specimens	...	63.61	36.39	21.60	13.38	1.41	3.59	22.39	100.79
Spent salmon. Male	35	75.27	24.73	19.24	4.37	1.12	3.06	19.15	99.91
" " Female	36	78.20	21.80	17.80	2.83	1.17	2.82	17.62	99.82
" " Average of 2 specimens	...	76.74	23.26	18.52	3.60	1.14	2.94	18.39	99.87

TABLE III.—*Continued.*

KIND OF FISH.	Laboratory Numbers of Specimens.	Water.	Water-free Substance.	Albuminoids, etc. (by difference).	Fats. Ether Extract.	Ash.	Nitrogen.	Protein, N × 6.25.	Water + Protein + Fats + Ash.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Spent land-locked salmon. Male	40	77.88	22.12	16.84	4.01	1.27	2.59	16.18	99.34
“ “ “ Female	41	79.20	20.80	17.65	1.95	1.20	2.76	17.24	99.59
“ “ “ Av. of 2 specimens	...	78.54	21.46	17.24	2.98	1.24	2.68	16.71	99.47
Lake trout	17	68.78	31.22	17.32	12.55	1.35	2.82	17.62	100.30
“	255	69.50	30.50	19.12	10.21	1.17	3.11	19.42	100.30
“ Average of 2 specimens	...	69.14	30.86	18.22	11.38	1.26	2.97	18.52	100.30
Brook trout	24	77.54	22.46	18.45	2.61	1.42	2.98	18.60	100.17
“	254	79.84	20.16	18.45	0.75	0.96	3.01	18.80	100.35
“	256	75.78	24.22	20.03	2.94	1.25	3.25	20.30	100.27
“ Average of 3 specimens	...	77.72	22.28	18.97	2.10	1.21	3.08	19.23	100.26
Pickerel	100	79.84	20.16	18.40	0.52	1.24	2.96	18.43	100.03
“	224	79.52	20.48	18.88	0.49	1.11	3.04	19.02	100.14
“ Average of 2 specimens	...	79.68	20.32	18.64	0.50	1.18	3.00	18.73	100.09
Pickerel. Pike	98	79.79	20.21	18.60	0.58	1.03	2.99	18.67	100.07
Mascalonge.	45	76.26	23.74	19.63	2.54	1.57	3.22	20.15	100.52
Eel, salt-water	4	69.80	30.20	18.95	10.34	0.91	3.08	19.25	100.30
“ “	217	73.40	26.60	17.61	7.88	1.11	2.84	17.75	100.14
“ “ Average of 2 specimens	...	71.60	28.40	18.28	9.11	1.01	2.96	18.50	100.22
Mullet	126	74.87	25.13	19.32	4.64	1.17	3.12	19.48	100.16
Mackerel	8	78.67	21.33	18.13	2.20	1.00	2.92	18.29	100.16
“	13	74.26	25.74	17.48	7.02	1.24	2.80	17.51	100.03
“	30	74.14	25.86	17.57	6.99	1.30	2.91	18.18	100.61
“	39	64.01	35.99	18.21	16.30	1.48	3.05	19.08	100.87
“	230	73.68	26.32	19.25	5.86	1.21	3.12	19.46	100.21
“	261	75.44	24.56	19.07	4.21	1.28	3.11	19.43	100.36
“ Average of 6 specimens	...	73.37	26.63	18.26	7.09	1.28	2.99	18.63	100.37
Spanish mackerel	43	68.10	31.90	20.97	9.43	1.50	3.43	21.45	100.48
Pompano	234	67.38	32.62	18.15	13.51	0.96	2.94	18.35	100.20
“	263	78.18	21.82	19.15	1.64	1.03	3.09	19.30	100.15
“ Average of 2 specimens	..	72.78	27.22	18.65	7.57	1.00	3.02	18.83	100.18
Blue fish	12	78.46	21.54	19.02	1.25	1.27	3.11	19.41	100.39
Butter fish	90	70.02	29.98	17.81	11.03	1.14	2.88	17.99	100.18
Large-mouthed black bass	53	78.61	21.39	19.24	0.96	1.19	3.11	19.44	100.20

Table III.—*Continued.*

Kind of Fish.	Laboratory Numbers of Specimens.	Water.	Water-free Substance.	Albuminoids, etc. (by difference).	Fats. Ether Extract.	Ash.	Nitrogen.	Protein, N × 6.25.	Water + Protein + Fats + Ash.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Small-mouthed black bass	91	74.82	25.18	21.50	2.44	1.24	3.47	21.71	100.21
Yellow perch	127	80.43	19.57	17.88	0.55	1.14	2.85	17.79	99.91
" "	208	78.07	21.93	19.47	1.12	1.34	3.15	19.69	100.22
" " Average of 2 specimens	...	79.25	20.75	18.68	0.83	1.24	3.00	18.81	100.13
Pike perch, Wall-eyed pike	52	79.74	20.26	18.42	0.47	1.37	2.97	18.58	100.16
Pike perch, Gray pike	257	80.85	19.15	17.26	0.76	1.13	2.86	17.88	100.62
Striped bass	7	79.02	20.98	18.26	1.56	1.16	2.99	18.69	100.43
" "	19	79.73	20.27	16.74	2.17	1.36	2.72	16.98	100.24
" "	225	77.27	22.73	18.81	2.81	1.11	3.04	18.97	100.16
" "	237	75.76	24.24	18.33	2.64	1.27	3.13	19.54	100.21
" "	248	77.87	22.13	18.81	2.20	1.12	3.04	18.97	100.16
" "	260	76.65	23.35	17.82	4.61	0.92	2.88	17.98	100.16
" " Average of 6 specimens	...	77.71	22.29	18.30	2.83	1.16	2.93	18.53	100.23
White perch	44	75.64	24.36	17.63	5.62	1.11	2.87	17.95	100.32
" "	46	75.77	24.23	20.43	2.52	1.28	3.29	20.58	100.15
" " Average of 2 specimens	...	75.71	24.29	19.03	4.07	1.19	3.08	19.27	100.24
Sea bass	251	79.32	20.68	18.75	0.49	1.44	3.17	19.84	101.09
Grouper	114	79.95	20.05	18.51	0.48	1.16	2.98	18.68	100.17
"	271	78.96	21.04	19.19	0.71	1.14	3.11	19.81	100.62
" Average of 2 specimens	...	79.40	20.55	18.85	0.60	1.15	3.04	19.25	100.40
Red snapper	20	78.22	21.78	19.89	0.62	1.27	3.23	20.17	100.28
" "	26	77.34	22.66	19.39	1.94	1.33	3.16	19.75	100.36
" "	242	79.81	20.19	18.31	0.54	1.34	3.08	19.26	100.95
" " Average of 3 specimens	...	78.46	21.54	19.20	1.03	1.31	3.16	19.73	100.53
Porgy	15	79.68	20.32	17.46	1.46	1.40	2.78	17.44	99.98
"	31	71.98	28.02	18.81	7.86	1.35	3.02	18.86	100.05
"	262	73.31	26.69	19.29	6.01	1.39	3.11	19.43	100.14
" Average of 3 specimens	...	74.99	25.01	18.52	5.11	1.38	2.97	18.58	100.06
Sheepshead	48	72.01	27.99	20.17	6.72	1.10	3.33	20.82	100.65
"	250	79.08	20.92	18.93	0.66	1.33	3.10	19.36	100.43
" Average of 2 specimens	...	75.55	24.45	19.54	3.69	1.22	3.22	20.08	100.54
Red bass	270	81.56	18.44	16.68	0.53	1.23	2.70	16.88	100.20
King fish	252	79.21	20.79	18.66	0.95	1.18	3.03	18.94	100.28

TABLE III.—*Concluded.*

KIND OF FISH.	Laboratory Numbers of Specimens.	Water.	Water-free Substance.	Albuminoids, etc. (by difference.)	Fats. Ether Extract.	Ash.	Nitrogen.	Protein, N × 6.25.	Water + Protein + Fats + Ash.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Weak fish	273	78.97	21.03	17.45	2.39	1.19	2.85	17.80	100.35
Black fish	38	76.95	23.05	18.96	2.81	1.28	3.09	19.33	100.37
"	205	81.36	18.64	17.44	0.55	0.65	2.82	17.61	100.17
"	244	79.64	20.36	18.71	0.62	1.03	3.03	18.91	100.20
"	269	78.44	21.56	18.76	1.44	1.36	3.03	18.96	100.20
" Average of 4 specimens	...	79.10	20.90	18.47	1.35	1.08	2.99	18.71	100.24
Hake	113	83.11	16.89	15.24	0.67	0.98	2.46	15.37	100.13
Cusk	110	82.01	17.99	16.92	0.17	0.90	2.72	17.00	100.08
Haddock	16	80.30	19.70	18.38	0.17	1.15	2.97	18.58	100.20
"	21	82.03	17.97	16.26	0.14	1.57	2.65	16.58	100.32
"	229	82.56	17.44	15.94	0.32	1.18	2.61	16.32	100.38
"	259	81.87	18.13	16.75	0.35	1.03	2.77	17.31	100.56
" Average of 4 specimens	...	81.69	18.31	16.83	0.25	1.23	2.75	17.20	100.37
Cod	3	83.48	16.52	14.97	0.28	1.27	2.48	15.49	100.52
"	11	83.39	16.61	14.95	0.40	1.26	2.58	16.09	101.14
"	206	80.71	19.29	17.59	0.30	1.40	2.93	18.32	100.73
"	228	83.43	16.57	15.26	0.31	1.00	2.54	15.84	100.58
"	243	82.20	17.80	16.08	0.51	1.21	2.69	16.80	100.72
" Average of 5 specimens.	...	82.64	17.36	15.77	0.36	1.23	2.54	16.51	100.74
Tom-cod	99	81.55	18.45	17.08	0.38	0.99	2.76	17.24	100.16
Pollock	81	76.02	23.98	21.65	0.78	1.55	3.46	21.60	99.95
Halibut	1	79.15	20.85	17.49	2.21	1.15	2.80	17.53	100.04
"	9	70.13	29.87	18.16	10.57	1.14	2.97	18.54	100.38
"	211	76.97	23.03	19.40	2.75	0.88	3.15	19.68	100.28
" Average of 3 specimens	...	75.42	24.58	18.35	5.17	1.06	2.97	18.58	100.23
Turbot	49	71.39	28.61	12.92	14.41	1.28	2.36	14.75	101.83
Common flounder.	2	83.37	16.63	14.73	0.62	1.28	2.39	14.91	100.18
" "	22	85.04	14.96	12.90	0.77	1.29	2.12	13.22	100.32
" " Average of 2 specimens	...	84.21	15.79	13.82	0.69	1.28	2.26	14.07	100.25
Winter flounder	253	84.35	15.65	14.01	0.44	1.20	2.33	14.53	100.52
Lamprey eel.	236	71.12	28.88	14.93	13.29	0.66	2.40	14.98	100.05
Skate	247	82.15	17.85	15.32	1.39	1.14	2.91	18.17	102.85

TABLE IV.

Sum of Protein (N × 6.25), Ether Extract, Ash, and Water in Flesh of Specimens of American Fishes.

Laboratory Number.	NAME.	Protein + Ether Extract + Ash in Water-free Substance.	Protein + Ether Extract + Ash + Water in Flesh.
		per ct.	per ct.
40	Spent land-locked salmon	97.01	99.34
41	“ “ “	98.00	99.59
	“ “ “ average	97.50	99.47
36	Spent salmon	99.15	99.82
35	“ “	99.61	99.91
	“ “ average	99.38	99.87
81	Pollock	99.74	99.95
236	Lamprey eel	100.18	100.05
15	Porgy	99.94	99.98
31	“	100.16	100.05
262	“	100.57	100.14
	“ average	100.22	100.06
127	Yellow perch	99.55	99.91
208	“ “	101.04	100.22
	“ “ average	100.29	100.13
110	Cusk	100.30	100.08
98	Pike pickerel	100.32	100.07
100	Pickerel	100.15	100.03
224	“	100.72	100.14
	“ average	100.43	100.09
258	Small-mouthed red horse	100.48	100.09
111	Cisco	100.59	100.14
126	Mullet	100.61	100.16
90	Butter fish	100.62	100.18
234	Pompano	100.60	100.20
263	“	100.70	100.15
	“ average	100.65	100.18
220	Alewife	100.70	100.18
5	“	100.77	100.20
	“ average	100.73	100.19
113	Hake	100.74	100.13
52	Pike perch, Wall-eyed pike	100.75	100.16
217	Salt-water eel	100.53	100.14
4	“ “ “	101.02	100.30
	“ “ “ average	100.77	100.22
91	Small-mouthed black bass	100.81	100.21
238	Sturgeon	100.81	100.15
99	Tom-cod	100.84	100.16
1	Halibut	100.18	100.04
211	“	101.19	100.28
9	“	101.30	100.38
	“ average	100.89	100.23
221	Shad	100.45	100.12
245	“	100.68	100.16
10	“	100.74	100.21
249	“	100.87	100.22
32	“	100.96	100.25
212	“	101.28	100.36
6	“	101.37	100.39
	“ average	100.91	100.27

TABLE IV.—*Continued.*

Laboratory Number.	NAME.	Protein + Ether Extract + Ash in Water-free Substance.	Protein + Ether Extract + Ash + Water in Flesh.
		per ct.	per ct.
53	Large-mouthed black bass	100.92	100.20
46	White perch	100.63	100.15
44	“ “	101.32	100.32
	“ “ average	100.97	100.24
17	Lake trout	100.97	100.30
255	“ “	101.01	100.30
	“ “ average	100.99	100.30
260	Striped bass	100.67	100.16
248	“ “	100.73	100.16
225	“ “	100.77	100.16
237	“ “	100.88	100.21
19	“ “	100.96	100.24
7	“ “	102.03	100.43
	“ “ average	101.00	100.23
269	Black fish	100.93	100.20
205	“	100.95	100.17
244	“	100.98	100.20
38	“	101.62	100.37
	“ average	101.12	100.24
270	Red bass	101.12	100.20
207	Smelt	99.17	99.82
23	“	103.09	100.62
	“ average	101.13	100.22
24	Brook trout	100.75	100.17
256	“ “	101.03	100.27
254	“ “	101.72	100.35
	“ “ average	101.17	100.26
252	King fish	101.29	100.28
13	Mackerel	100.15	100.03
8	“	100.73	100.16
230	“	100.94	100.21
261	“	101.46	100.36
30	“	102.37	100.61
39	“	102.39	100.87
	“ average	101.34	100.37
43	Spanish mackerel	101.52	100.48
273	Weak fish	101.64	100.35
2	Common flounder	101.09	100.18
22	“ “	102.19	100.32
	“ “ average	101.64	100.25
233	California salmon	101.67	100.60
12	Blue fish	101.83	100.39
16	Haddock	100.92	100.20
21	“	101.81	100.32
229	“	102.16	100.38
259	“	103.08	100.56
	“ average	101.99	100.37
114	Grouper	101.18	100.17
271	“	102.94	100.62
	“ average	102.06	100.40
47	Herring	102.07	100.66
280	Salmon	100.82	100.32

TABLE IV.—*Continued.*

Laboratory Number.	NAME.	Protein + Ether Extract + Ash in Water-free Substance.	Protein + Ether Extract + Ash + Water in Flesh.
		per ct.	per ct.
14	Salmon	101.10	100.46
279	“	101.27	100.49
78	“	103.08	101.07
77	“	104.43	101.62
	“ average	102.14	100.79
45	Mascalonge	102.20	100.52
250	Sheepshead	102.08	100.43
48	“	102.33	100.65
	“ average	102.20	100.54
20	Red snapper	101.30	100.28
26	“ “	101.69	100.36
242	“ “	104.53	100.95
	“ “ average	102.50	100.53
18	White fish	102.87	100.87
257	Pike perch, Gray pike	103.23	100.62
253	Winter flounder	103.41	100.52
3	Cod	103.03	100.52
228	“	103.55	100.58
206	“	103.76	100.73
243	“	104.22	100.72
11	“	106.87	101.14
	“ average	104.28	100.74
251	Sea bass	105.04	101.09
49	Turbot	106.39	101.83
247	Skate	116.01	102.85
	PRESERVED FISH.		
79	Desiccated cod, flesh desiccated and ground, dried	104.02	103.41
42	Mackerel, salted	98.40	99.08
34	Salt cod, salted and dried	107.98	103.70
37	“ “ “ “	109.06	104.19
	“ “ “ “ average	108.57	103.95
88	Haddock, salted, smoked and dried	98.60	99.61
218	Halibut, “ “ “	100.03	100.01
28	“ “ “ “	100.66	100.34
	“ average	100.35	100.18
33	Herring	100.77	100.50
87	Sardines, canned	98.99	99.56
94	Mackerel, canned	99.13	99.72
95	Salt mackerel, canned	99.56	99.74
219	“ “ “	100.33	100.19
	“ “ “ average	99.95	99.97
29	Salmon, canned	99.33	99.77
241	“ “	100.65	100.27
96	“ “	100.89	100.33
	“ “ average	100.29	100.12
240	Tunny, “Horse mackerel,” canned	100.53	100.15
275	Smoked haddock, canned	101.57	100.51

[*To be concluded in next number.*]

REVIEWS AND REPORTS.

The Arrangement of Atoms in Space in Organic Molecules.[1]

The expression "chemical structure" as commonly used by chemists has, as is well known, nothing to do with the arrangement of atoms in space. The structural formula does not profess to represent spatial relations, but simply the connections which, after a careful study of the transformations and modes of formation of the compound represented, are believed to exist between the atoms. Nevertheless, although we do not commonly consider the question of space relations, it is clear that atoms must have some definite positions in space in the molecules, and the only reason why we do not represent these positions is because we know practically nothing about them. The most definite suggestion concerning space relations of atoms which has been made is that of Le Bel and Van't Hoff. The well known hypothesis of these authors was put forward to account for a certain kind of so-called physical isomerism which shows itself in the action of substances upon polarised light. Since this hypothesis was proposed, the number of cases of "abnormal isomerism," that is to say, of cases of isomerism which cannot be accounted for by the commonly accepted method of explaining structure, has increased to a considerable extent, and the necessity for some new hypothesis, or for some modification of the old ones, has come to be pretty generally recognised. Among the cases of isomerism which it is at least difficult to explain by the aid of the prevailing views are those of maleic and fumaric acids; citraconic and mesaconic acids; certain halogen derivatives of crotonic acid and of cinnamic acid; and coumaric and coumarinic acids. More than one hypothesis has been proposed to account for these cases of isomerism, but no one has shown itself to be entirely satisfactory. Quite recently Johannes Wislicenus, Professor of Chemistry in the University of Leipsic, has made what has the appearance of being an important contribution towards the solution of the problem referred to. The author shows that many of the facts known in regard to the relations between maleic and fumaric acids, and the other substances which furnish examples of "abnormal isomerism," may be explained by the aid of an extension of the Le Bel–Van't Hoff hypothesis. It is difficult without the aid of models to give a clear idea concerning the hypothesis of Wislicenus, but some idea of it may be gained from the following. If we suppose a carbon atom to exert its affinities in the directions of the solid angles of a tetrahedron, as is done in the Le Bel-Van't Hoff hypothesis, then, when two carbon atoms unite, as in ethane, the union will be between two solid angles of two tetrahedrons. If the two carbon atoms unite by the ethylene kind of union, the union will be along a line corresponding to one of the edges of each tetrahedron. In the former case, in which single union exists, the two parts of the molecule represented by the two tetrahedrons can be supposed to be capable of revolving around an axis either in the same direction or in opposite directions. This axis corresponds to the straight line joining the two carbon atoms. In the case in which double union exists no such revolution is possible. Again if, by addition to an unsaturated compound like ethylene, a saturated compound is formed, the kind of union between the carbon atoms is changed, and the possibility of revolution of the two parts of the compound is given. Whether such revolution take place or not will be determined largely by the structure of the compound. The tendency will be for those parts of the molecule which have the greatest specific affinity for one another to take those positions in which they are nearest to one another. Thus, suppose that chlorine is added to ethylene. By following the change on the model, it is seen that in the resulting figure the two chlorine atoms in ethylene chloride are situated at angles of the two tetrahedrons which are nearest each other. But chlorine has a stronger affinity for hydrogen than it has for chlorine, and therefore each chlorine atom would tend to get as near a hydrogen atom as possible. This involves a partial revolution of the two tetrahedrons in opposite directions around their common axis. So also hydrogen would tend to take a position as near as possible to hydroxyl and to carboxyl, while hydroxyl would avoid hydroxyl, and carboxyl would avoid carboxyl. These views are suggested as a result of a careful application of the original Le Bel-Van't Hoff hypothesis, and are, of course, of little value unless they can be shown to be in accordance with the facts.

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[1] **Ueber die räumliche Anordnung der Atome in organischen Molekulen, und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen. Von Johannes Wislicenus.—Abhandlungen der mathematisch-physischen Klasse der Königl. Sächsischen Gesellschaft der Wissenschaften. Band XIV, No. 1.**

The chief merit of the work of Wislicenus consists in the fact that he has shown that a large number of phenomena which have been observed in the study of such cases of isomerism as were mentioned above, find a ready explanation in terms of the new hypothesis, whereas for most of these phenomena no explanation whatever has thus far been presented. The most marked case presented is that of maleic and fumaric acids. One by one the author discusses the transformations of these acids and their substitution products, and he comes to this conclusion: "There is not to my knowledge a single fact known in regard to the relations between fumaric and maleic acids which is not explained by the aid of the above geometrical considerations, not one which does not clearly support the new hypothesis." Among the facts which he discusses in the light of the hypothesis are these: The formation of fumaric and maleic acids from malic acid; the quantitative transformation of maleic into fumaric acid by contact with strong acids;

the transformation of the ethereal salts of maleic acid into those of fumaric acid by the action of a minute quantity of free iodine; the formation of brommaleic acid and hydrobromic acid from the dibromsuccinic acid formed by the addition of two bromine atoms to fumaric acid; the formation of dibromsuccinic acid from brommaleic acid, and of isodibromsuccinic acid from bromfumaric acid by the action of fuming hydrobromic acid; the conversion of brommaleic acid into fumaric and then into succinic acid by the action of sodium amalgam; the formation of one and the same tribromsuccinic acid by the action of bromine on brommaleic and on bromfumaric acid; and finally, the conversion of maleic into inactive tartaric acid, and of fumaric into racemic acid by potassium permanganate. All these facts are shown to find a ready explanation by the aid of the new hypothesis. Further, it is shown that the decompositions of the salts of certain halogen derivatives of organic acids, which give up halogen salt and carbon dioxide, as well as the formation of lactones and of anhydrides of dibasic acids, are in perfect harmony with the hypothesis. But the only way to get a clear conception in regard to the mass of material which the author has brought together and which he has shown to support his hypothesis is by a careful study of the original paper, and the object of this notice is mainly to call the attention of American chemists to it.

As to the question what value to attach to the speculations which Wislicenus has brought to our notice it is difficult to give any but a general answer. No one can well have a greater fear of mere speculation, which is indulged in independently of the facts, than the writer of this notice. Great harm has been done chemistry, and probably every other branch of knowledge, by unwarranted speculation, and every one who has looked into the matter knows how extremely difficult it is to emancipate one's self from the influence of a plausible hypothesis even when it can be shown that it is not in accordance with the facts. It behooves every one, therefore, before accepting a new hypothesis, no matter how fascinating it may appear at first sight, to look carefully into the facts, and to endeavor to determine independently whether it is well founded or not. On the other hand, there is some danger to be apprehended from a tendency, sometimes observed, to denounce everything speculative, no matter how broad the basis of facts upon which it rests may be. Without legitimate speculation it is clear that there could be no great progress in any subject. As far as the hypothesis under consideration is concerned, the writer is firmly of the opinion that it is likely to prove of great value in dealing with a large number of chemical facts, and that, as it suggests many lines of research, it will undoubtedly in the course of a few years exert a profound influence on chemistry. Whether the evidence which will be accumulated will or will not confirm the view that the tetrahedron form is characteristic of the simplest molecules of carbon compounds is not the most important question to be asked under the circumstances. We should rather ask whether the testing of the hypothesis is or is not likely to bring us nearer to the truth. It is a proposition that admits of no denial that a hypothesis which can be tested by experiment, and which suggests lines of work and stimulates workers to follow them, is a gain to science no matter what the ultimate fate of the hypothesis may be.

PRINCIPIEN DER ORGANISCHEN CHEMIE. Von Dr. Eugen Lellmann, Privatdocent der Chemie an der Universität Tübingen. Berlin: Verlag von Robert Oppenheim, 1887. 511 pp. 8vo.

The author of this book has brought together all reactions of carbon compounds which have anything like a general character and treated them systematically. The book is intended not as a text-book of organic chemistry, but rather as a supplement to the larger books on this subject, the object being especially to emphasise the synthetical reactions and to point out the relations between these reactions, and the generalisations which the facts now in our possession justify. No similar attempt has been previously made, so that the author has had to rely entirely upon his own ingenuity in classifying the reactions. In his treatment they fall under four heads: I. Reactions in which the number of carbon atoms in a compound is not changed; II. Building up of a compound with a larger number of carbon atoms from such as contain a smaller number; III. Decomposition of a compound into several others, each of which contains a smaller number of carbon atoms; and IV. Action of two carbon compounds upon each other, resulting in the formation of two new organic substances. Under I the following sub-classes of reactions are treated: (1) Molecular rearrangements; (2) Addition of elements or inorganic compounds to organic compounds; (3) Splitting off of elements or inorganic compounds from organic compounds; (4) Substitution phenomena. Under II are the following: (1) Addition of two organic compounds to each other; (2) Addition of two organic compounds to each other accompanied by the taking up of an element; (3) Separation of the constituents of an inorganic compound from several organic compounds and union of the organic residues; (4) Separation of constituents from several organic compounds caused by the action of elements, and union of the organic residues. Under III there are taken up: (1) Simple decomposition of an organic compound into several others; (2) Decomposition of an organic compound into several others preceded by the taking up an element or of the constituents of an inorganic compound.

The book is enriched by references to the important sources of information down to January 1, 1885, and later articles which appeared while the book was passing through the press have also been considered as far as possible. It is clearly written, and will be of assistance in helping students to take a broad view of the chemical changes with which they are constantly dealing. In the usual method of treatment the individual reactions are necessarily kept in the foreground, and interesting and important generalisations are to a great extent lost sight of; indeed, it is only after one has acquired a pretty thorough knowledge of the various reactions met with that generalisations in regard to them have any significance. Advanced students are earnestly advised to study Dr. Lellmann's book with care.

THE PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS. By Ira Remsen. Third edition, enlarged and thoroughly revised. Philadelphia: Lea Brothers & Co., 1887. 318 pp. 12mo.

This book has been enlarged from 242 to 318 pages, and has also been rewritten to a large extent. In the preface the author says: "The chapter on valence has been almost entirely rewritten and at the same time enlarged, and I feel that the treatment of the subject is now much more satisfactory than in the earlier editions. A brief introductory chapter, and chapters on matters pertaining to the subject of chemical affinity, and the connection between constitution and chemical conduct, have been added, and many other additions have been made throughout the book.

"The treatment of the subject of chemical affinity and allied subjects is purposely as brief and simple as possible, the object being mainly to interest the student, in the field of which but a glimpse is given, and to give a general idea of the results which have recently been reached."

DIE KÜNSTLICHEN ORGANISCHEN FARBSTOFFE. Unter Zugrundelegung von sechs Vorlesungen, gehalten von Prof. Dr. E. Noelting, Director der "École de Chimie" in Mühlhausen, bearbeitet von Dr. Paul Julius. Berlin: R. Gaertner, 1887. 235 pp.

The number of organic dye-stuffs is increasing so rapidly that it is almost impossible for one to keep thoroughly informed, even in regard to those which are described in scientific journals. But in addition many others are constantly being made and patented, and not described in the regular journals. Information in regard to the latter can usually be obtained only from the descriptions of patents in the different countries. The need of a connected treatise on these compounds is obvious, and recently two small books have appeared having the organic dye-stuffs as their subject. The book before us is admirably arranged, and gives in a small space a clear treatment of the many dye-stuffs and the relations existing between them. The first chapter treats of coal tar and the chemistry of benzene and its derivatives. The second, of the intermediate products in the preparation of dye stuffs. These are the derivatives of the hydrocarbons which must be made in order to get the dye-stuffs themselves, as, for example, nitrobenzene, aniline, toluidine, phthalic acid, benzoic aldehyde, resorcin, pyrogallol, etc. The theory in regard to the cause of the coloring properties of certain organic compounds is next considered, and then in succeeding chapters the most important dye-stuffs are taken up.

Recent Advances in the Chemistry of Manganese, and a New Determination of the Atomic Weight of Fluorine.

Up to the present time, five oxides of manganese have been known: Manganous oxide, MnO; red manganese oxide, Mn_3O_4; manganic oxide, Mn_2O_3; manganese dioxide, MnO_2; and manganese heptoxide, Mn_2O_7. From some recent investigations which have been carried on by Franke,[1] it appears that two new members must now be added to this list.

Manganese trioxide, MnO_3.—When potassium permanganate is added to well-cooled concentrated sulphuric acid it dissolves with a beautiful green color, and if to this cool solution either an excess of the permanganate or a small quantity of water be added, a heavy liquid of a metallic lustre separates, which Aschoff has shown to be the heptoxide of manganese, Mn_2O_7. On the other hand, when this green solution to which a small quantity of water has been added is warmed cautiously to 40°-50°, a *beautiful violet-colored gas* is evolved, which Franke has found to have the composition MnO_3.

The action of the sulphuric acid on potassium permanganate he believes can be rightly expressed by the following equations:

I. $2KOMnO_3 + H_2SO_4 = K_2SO_4 + 2OH . MnO_3$.
II. $2OH . MnO_3 + H_2SO_4 = (MnO_3)_2 . SO_4 + H_2O$.
Kept cold: $(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4$.
Warmed to 30°: $(MnO_3)_2SO_4 + H_2O = 2MnO_3 + H_2SO_4 + O$.

The oxysulphate of manganese, $(MnO_3)_2SO_4$, which he regards as the intermediate product in these reactions, has not been shown to exist in the sulphuric acid solution of potassium permanganate, though some strictly analogous compounds are known. These are the manganese oxychloride of Aschoff, MnO_3Cl, and the manganese oxyfluoride of Wöhler, MnO_3F; so that it is safe to assume the existence of a corresponding oxysulphate. A still more convenient method of preparation, and one by which the gas can be obtained in larger quantities and purer condition, consists in treating the oxysulphate solution with potassium carbonate:

$$(MnO_3)_2SO_4 + K_2CO_3 = 2MnO_3 + K_2SO_4 + CO_2 + O.$$

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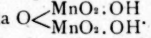
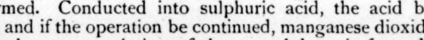
[1] Journal für praktische Chemie **36**, 31.

20 cc. of the oxysulphate solution, which is best made by dissolving 5 to 8 grams of potassium permanganate in concentrated sulphuric acid, is allowed to flow drop by drop into a small flask containing 10 grams of dry potassium carbonate. The gases evolved in this reaction are conducted through a U-tube, which is surrounded by a freezing mixture. The oxide thus obtained, and which at ordinary temperatures is a violet-colored gas, condenses in the U-tube to a dark red, amorphous mass. It has a peculiar odor, and attacks the mucous membranes of the throat and nose, producing a cough. When heated gradually to 50° C. the dark red amorphous mass is transformed into a violet-colored vapor with partial decomposition into manganese dioxide and oxygen. When heated suddenly or to a temperature higher than 50° C. it breaks down completely into manganese dioxide and oxygen. It dissolves with difficulty in water, and this solution is found to contain free manganic acid; this, however, soon decomposes, manganese dioxide and oxygen are set free, and a new acid, dimanganic acid, is formed. This probably has the composition and structure represented by the formula  $\mathrm{O}<\substack{\mathrm{MnO_2.OH}\\ \mathrm{MnO_2.OH}}$. When the violet gas is conducted into solutions of caustic potash or soda it dissolves with a green color, and the manganates of these metals are formed. Conducted into sulphuric acid, the acid becomes yellow, and if the operation be continued, manganese dioxide separates and a green solution of the oxysulphate is formed. This trioxide, MnO_3, is an exceedingly powerful oxidising agent; it oxidises hydrochloric acid, as do the other oxides of manganese, with the formation of chlorine. The new oxide possesses a remarkable coloring power, 0.0050 gram of the substance being sufficient to cover the inside of a litre flask with an intense red color.

Manganese tetroxide, MnO_4.—When moist carbon dioxide gas is conducted over the oxysulphate solution there is formed, in addition to the oxide just described, a quantity of a blue gas, which Franke believes to be the tetroxide of manganese, MnO_4. This blue gas is condensed by cold to a bluish-violet amorphous substance which is more volatile than the trioxide MnO_3. It dissolves in water less readily than the trioxide, and differs from it in other ways. Up to the present, such small quantities of this substance have been obtained that it has been impossible to determine its composition by analysis. Nevertheless, the properties and reactions of the substance point to the formula MnO_4, and the formation of the tetroxide from the oxysulphate solution is probably to be represented in this way:



$$\substack{\mathrm{MnO_3}\\ \mathrm{MnO_3}}>\mathrm{SO_4} + \mathrm{H_2O} = \mathrm{MnO_4} + \mathrm{MnO_3} + \mathrm{H_2SO_4}.$$

The Higher Chlorides of Manganese.—Nicklès[1] was the first to study the action of dry hydrochloric acid gas on manganese dioxide in the presence of anhydrous ether, and he came to the conclusion that manganese tetrachloride is formed in this way, and that this combines with the ether and with the water formed during the reaction to form a violet-colored compound of the formula $MnCl_4 + 12(C_2H_5)_2O + 2H_2O$. Christensen[1] has recently taken up the study of the action of dry hydrochloric acid on manganese dioxide and manganic oxide, Mn_2O_3, in the presence of ether, and has reached results differing considerably from those of Nicklès. He does not attempt the complete analysis of the compounds formed, as they cannot be obtained in pure condition; but, by determining the relation between the quantity of *active chlorine* and manganese in these compounds, he is led to more correct views regarding their composition. In manganese tetrachloride, $MnCl_4$, for example, the atomic ratio between the manganese and the *active chlorine* is 1 : 2, whereas in manganic chloride, Mn_2Cl_6, the ratio is 11 : 1. This ratio can be determined approximately even in the presence of an excess of hydrochloric acid or of organic compounds containing chlorine. The results are briefly these: When dry hydrochloric acid acts on manganese dioxide and manganic oxide in the presence of ether, at ordinary temperatures, the compound formed is the same in both cases, and the ratio between the manganese and active chlorine corresponds to that required by the formula Mn_2Cl_6, that is, as 1 : 1. At low temperatures (—10°) manganese tetrachloride seems to be the main product of the reaction. When the ether contains but a small quantity of hydrochloric acid a blue solution is formed, which becomes green on the addition of more hydrochloric acid. Christensen supposes this change of color to be due to the formation of a hydrated salt from one containing no water, and that there are two chlorides of manganese, viz. Mn_2Cl_6 and $Mn_2Cl_6 + xH_2O$, which correspond to the analogous chromic chlorides, Cr_2Cl_6 and $Cr_2Cl_6 + 12H_2O$.

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[1] Annales de Chim. et de Phys. [4], **5**, 161.

Franke[2] claims that this explanation of the change in color is not supported by facts, and shows that the blue solution contains manganese tetrachloride, which changes into the green compound by taking up hydrochloric acid directly, forming the compound $\begin{matrix}HCl\\HCl\end{matrix}{>}MnCl_4$. In other respects Franke's work confirms the results obtained by Christensen.

Compounds of Manganese and Fluorine.—Christensen has also been engaged of late in studying the action of hydrofluoric acid on the oxides and hydroxides of manganese.

Manganic fluoride, $Mn_2F_6 + 6H_2O$.—When pure manganese dioxide is treated with hydrofluoric acid this compound is formed. It crystallises in dark brown prisms. It can also be formed by dissolving manganite, H_2MnO_4, in hydrofluoric acid. When manganic fluoride is treated with a concentrated solution of potassium fluoride, a beautiful rose-red double salt of the composition $4KF . Mn_2F_6 + 2H_2O$ crystallises out. The salt can be more easily prepared by fusing acid potassium fluoride, HF.KF, with manganese dioxide. This salt was prepared some time ago by Nicklès, who assigned to it the formula $2KF.MnF_4$, and considered it as a salt of the acid H_2MnF_6, which he regarded as the analogue of hydrofluosilicic acid. This view, according to Christensen, is untenable, and we must, according to him, regard the salt as analogous to certain double fluorides and chlorides which occur in nature. These belong to the general type $4RF.M_2F_6$; and all of Christensen's experiments tend to show that *manganic oxide,* Mn_2O_3, *is strictly analogous to the corresponding oxides of aluminium and iron.*

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[1] Journal für praktische Chemie **35**, 57.

[2] *Ibid.* **36**, 38.

The corresponding double salt of manganese and ammonium, $4NH_4F.Mn_2F_6$, can be easily prepared in pure condition, and has been used by Christensen in the redetermination of the atomic weight of fluorine. These determinations are based upon the determination of *active fluorine* in the compound, and his best results give as the atomic weight of fluorine, 18.91, 18.94, 18.95, 18.91 and 18.94 respectively. For $H = 1$ the atomic weight of fluorine is therefore 18.94. For $O = 16$ we have $F = 18.99$, or very nearly 19.0. J. H. K.

NOTES.

The Constitution of Selenious Acid.

In nearly all the attempts that have recently been made to determine the constitution of inorganic compounds, the organic derivatives of these compounds have generally played an important part. Thus the constitution of the platinum bases was determined by Jörgensen by introducing pyridine in the place of ammonia; phosphorus was shown to be pentavalent by La Coste and Michaelis, who prepared the isomeric compounds $(C_6H_5)_3PO$ and $(C_6H_5)_2P(OC_6H_5)$; triphenyl bismuth bromide, $(C_6H_5)_3BiBr_2$, prepared by Polis and Michaelis, proved bismuth to be also pentavalent. Particularly in the investigations on the constitution of the inorganic acids, such as phosphorous and sulphurous acids, have the organic derivatives been used.

It is now pretty well settled that the hypothetical sulphurous acid obtained from the sulphites is the so-called unsymmetrical acid $H.SO_2.OH$, and not the normal or symmetrical dihydroxyl acid $SO(OH)_2$. This has been shown, on the one hand, by the fact that the alkyl iodides and alkali sulphites react to form salts of alkyl sulphonic acid, in which the alkyl residue is undoubtedly connected with the sulphur—

$$K_2SO_3 + C_2H_5I = C_2H_5SO_3K + KI,$$

and, on the other hand, by the formation of the ethyl salt of ethylsulphuric acid by the action of ethyl iodide upon silver sulphite,

$$Ag_2SO_3 + 2C_2H_5I = C_2H_5SO_2OC_2H_5 + 2AgI;$$

while, by the action of alcohol on thioxyl chloride, the ethyl salt of sulphurous acid, $(C_2H_5O)_2SO$, isomeric with the preceding, is formed—

$$SOCl_2 + 2C_2H_5OH = SO(OC_2H_5)_2 + 2HCl.$$

Michaelis and Landmann[1] now take up the question of the constitution of selenious acid, and find that it must be regarded as having a constitution entirely different from that of sulphurous acid, and that it is a true dihydroxyl acid, $SeO(OH)_2$. This they show by the fact that potassium selenite conducts itself toward ethyl iodide in an entirely different manner from potassium sulphite. Instead of a salt corresponding to an alkyl sulphonic acid being formed, all the selenium is precipitated in the free state. The ethereal salts made, on the one hand, from ethyl iodide and silver selenite,

$$2C_2H_5I + Ag_2SeO_3 = (C_2H_5O)_2SeO + 2AgI,$$

and, on the other, from sodium ethylate and selenyl chloride,

$$2C_2H_5ONa + SeOCl_2 = 2NaCl + SeO(OC_2H_5)_2,$$

were then compared and found to be identical in every respect. It hence follows that the ethereal salt made in both ways has the same constitution, $SeO(OC_2H_5)_2$. The selenites have accordingly the constitution $SeO(OM)_2$, and selenious acid is a true dihydroxyl acid, $SeO{<}^{OH}_{OH}$, and in this respect differs markedly from sulphurous acid.

W. R. O.

Professor Wolcott Gibbs has resigned the Rumford Professorship in Harvard University in order to devote himself exclusively to research. He has removed to Newport, R. I., where he is erecting a private laboratory.

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[1] Annalen der Chemie **241**, 150.